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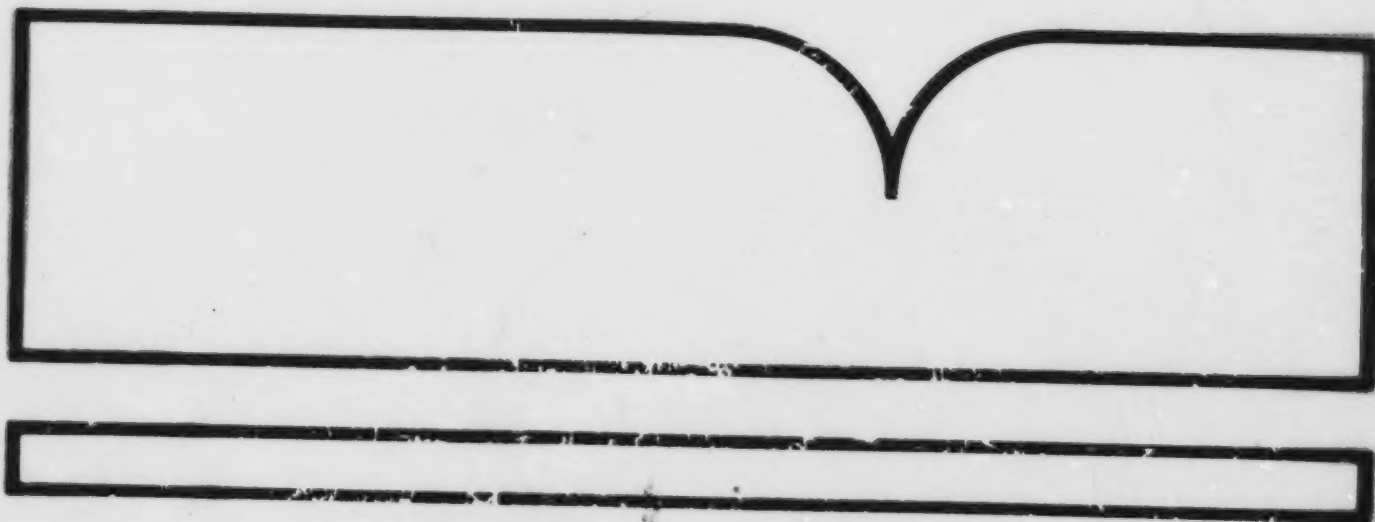
Determination of the Thermal
Decomposition Properties of 20 Selected
Hazardous Organic Compounds

Dayton Univ., OH

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Aug 84



U.S. Department of Commerce
National Technical Information Service

NTIS

DETERMINATION OF THE THERMAL DECOMPOSITION
PROPERTIES OF 20 SELECTED HAZARDOUS ORGANIC COMPOUNDS

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CR-807815

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CINCINNATI, OH 45268

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-84-138	2.	3. RECIPIENT'S ACCESSION NO. P88 A 232487
4. TITLE AND SUBTITLE Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds	5. REPORT DATE August 1984	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Barry Dellinger, Juan L. Torres, Wayne A. Rubey, Douglas L. Hall, and John L. Graham	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Dayton Research Institute 300 College Park Dayton, OH 45469	10. PROGRAM ELEMENT NO. D 109	
	11. CONTRACT/GRANT NO. CR-807815	
12. SPONSORING AGENCY NAME AND ADDRESS US-EPA/IERL-Ci Incineration Research Branch Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Research	
	14. SPONSORING AGENCY CODE EPA/600/12	
15. SUPPLEMENTARY NOTES		
16. ABSTRACT Laboratory determined thermal decomposition profiles and kinetic data for a list of 20 selected hazardous organic compounds are reported. All data were obtained in flowing air at mean gas-phase, high-temperature zone residence times ranging from one to six seconds. The extrapolated temperatures required for 99.99% destruction of the parent compound at two seconds mean residence time, $T_{99.99}(2)$, ranged from 600°C for 1,1,1-trichloroethane to 950°C for acetonitrile. The process and parameters potentially controlling incineration efficiency are discussed, and four previously proposed methods of ranking compound incinerability are critically reviewed.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 204
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related polluttional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The permanent, safe disposal of industrial waste containing hazardous organic material is of vital importance. This report presents the results of a laboratory study of the thermal decomposition properties of selected hazardous organic compounds. The thermal decomposition profiles and kinetic data for a list of 20 organic compounds are reported, and the possible chemical mechanisms responsible for their thermal destruction are discussed. Processes and parameters potentially controlling incineration efficiency and formation of products of incomplete combustion are also examined. The information presented in this report should be of value in determining the relative incinerability of hazardous organic waste materials.

Requests for further information regarding laboratory derived thermal decomposition of hazardous waste compounds and their kinetic behavior should be directed to the Incineration Research Branch, IERL, Cincinnati.

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ABSTRACT

Laboratory determined thermal decomposition profiles and kinetic data for a list of 20 selected hazardous organic compounds are reported. All data were obtained in flowing air at mean gas-phase, high-temperature zone residence times ranging from one to six seconds. The extrapolated temperatures required for 99.99% destruction of the parent compound at two seconds mean residence time, $T_{99.99(2)}$, ranged from 600°C for 1,1,1-trichloroethane to 950°C for acetonitrile. The processes and parameters potentially controlling incineration efficiency are discussed, and four previously proposed methods of ranking compound incinerability are critically reviewed.

This report was submitted in fulfillment of CR-807815 by the University of Dayton under the (partial) sponsorship of the U.S. Environmental Protection Agency. This report covers the period from July, 1980, to July, 1983, and work was completed as of July, 1983.

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LIST OF ABBREVIATIONS AND SYMBOLS

- A - Arrhenius coefficient (s^{-1})
- $\text{\AA}$ - Angstrom
- a - Stoichiometric reaction coefficient for compound A for oxidation, or reaction order for compound A
- α - Stoichiometric reaction coefficient for compound A for pyrolysis, or reaction order for compound A
- [A] - Concentration of species A at time t
- [A]₀ - Initial concentration of species A
- A_{∞} - Arrhenius coefficient in the high pressure limit
- AIT - Autoignition temperature ($^{\circ}\text{C}$)
- atm - Atmosphere
- b - Stoichiometric reaction coefficient for O_2 for oxidation of A, or reaction order for O_2
- B.P.^{760mm} - Boiling point at 760 mm of mercury pressure
- $^{\circ}\text{C}$ - Degrees centigrade
- CFR - Code of Federal Regulations
- CH_3 - Methyl radical
- Cl - Chlorine atom (radical)
- Cl_2 - Chlorine molecule
- ClO - Chloroxy radical
- cm - Centimeter
- CO - Carbon monoxide
- CO_2 - Carbon dioxide
- D - Effective gas phase diffusion coefficient
- DE - Destruction efficiency
- DE ($\tau_1, \tau_2, \dots, \tau_n$) - Destruction efficiency as a function of variables τ through τ_n
- DRE - Destruction and removal efficiency
- E_a - Activation energy (kcal mole^{-1})

E_{∞} - Activation energy in the high pressure limit
 FID - Flame ionization detector
 f_r - Fraction remaining
 $\bar{f}_r$ - Midpoint fraction remaining over the interval Δf_r
 Δf_r - Interval of change of f_r
 $g(\tau_1)$ - Distribution function for variable τ_1
 GC-MS - Gas chromatography-mass spectrometry
 H - Hydrogen atom (radical)
 H_2O - Water
 H_C - Molar heat of combustion (kcal mole⁻¹)
 H_C/gram - Heat of combustion (per gram molecular weight) equals the molar heat of combustion of a substance divided by its molecular weight (kcal g⁻¹)
 HCl - Hydrochloric acid
 HRGC - High resolution gas chromatography
 ID - Inside diameter
 °K - Degrees Kelvin
 k - Rate constant for overall destruction of parent species
 k_1 - Global pyrolysis rate constant
 k_2 - Global oxidation rate constant
 k_2' - Pseudo-first order rate constant (s⁻¹)
 L - Length of combustion zone
 ln - natural logarithm
 M - Molar concentration
 m - Meter
 M.P. - Melting point
 μl - Microliter
 O - Oxygen atom (radical)
 O_2 - Oxygen molecule
 OH - Hydroxyl radical
 PICs - Products of incomplete combustion
 POHCs - Principle organic hazardous constituents
 P_i - Probability of O_2 concentration $CO_{2,i}$ and residence time $t_{r,i}$
 R - Universal gas constant (1.99 cal mole⁻¹, °K⁻¹)
 r^2 - Coefficient of correlation
 subl - Sublimation point
 T - Temperature

t_c - Chemical reaction time
 t_d - Mixing time
TDAS - Thermal decomposition analytical system
 T_{DE} - Temperature required for destruction efficiency DE
TDU - Thermal decomposition unit
TDU-GC - Thermal decomposition unit-gas chromatograph
 $T_{onset}(2)$ - Temperature for onset of thermal destruction at
2.0 seconds mean residence time ($^{\circ}C$)
 $\bar{t}_r$ - Mean gas phase residence time (s)
 $T_{99}(2)$ - Temperature for 99% destruction of parent material
at 2.0 seconds mean residence time ($^{\circ}C$)
 $T_{99.99}(2)$ - Temperature for 99.99% destruction efficiency of
parent material at 2.0 seconds mean residence time ($^{\circ}C$)
UDRI - University of Dayton Research Institute
 V - Average gas velocity
wt% - Weight percent

ACKNOWLEDGMENTS

It is with pleasure that we acknowledge the efforts of our colleague, Mr. John Duchak, who assisted in, or personally generated, some of the thermal decomposition data. We gratefully acknowledge the advice, practical knowledge, and patience of our EPA Project Officer, Mr. Richard A. Carnes, who has supported and fought many battles with us.

We also acknowledge the efforts of Mr. Trevor Bridle, EPS; Mr. Myron Malanchuk, EPA; Dr. William Randall Seeker, EER; and Dr. Wing Tsang, NBS, for their review and comments concerning this report.

SECTION 1

INTRODUCTION

Regulations enacted under the Resource Conservation and Recovery Act (RCRA) of 1976 have made the traditional methods of hazardous waste disposal, such as impounding and landfilling, less desirable due to increased expense and legal responsibility for public safety. Consequently, there are increasingly strong economic incentives to completely destroy these materials and thus avoid financial responsibility for the possible deleterious environmental effects caused by the storage of these materials.

Alternative destruction techniques may be classified as chemical or thermal. Chemical destruction techniques are usually specific to the compound being disposed while thermal techniques such as incineration are more generally applicable to the destruction of all hazardous organic wastes. Incineration, although initially costly, is desirable since it permanently disposes of all parent materials except for a very few volatile inorganics and reduces the residual waste volume to an extremely low level which may be handled easily and relatively inexpensively.

There exists a clear urgency in all sectors; the public, industry, government, and academia to develop to the fullest extent possible the science of incineration. Historically, incinerators have been designed and their operating parameters have been developed through experience and additional trial and error. Admittedly, the complete destruction by thermal decomposition of a complex mixture of waste organic materials (many components of which are unidentified) presents a difficult problem to any scientist or engineer who must address the question. This task is further complicated by the diverse physical forms of organic waste and the various incineration system designs available.

The ultimate goal of incineration is to destroy a waste with as high a destruction efficiency (DE) as possible. Under RCRA, an incinerator operator must show that the facility can adequately destroy those hazardous waste constituents which are most difficult to incinerate (1). In theory, the permit writer will select compounds within the mixture which are of sufficient toxicity, concentration, and thermal stability so as to be designated as principal organic hazardous constituents (POHCs). It must then be shown, possibly by trial burn, that the designated POHCs can be destroyed or removed by the particular incineration system to a destruction and removal efficiency (DRE) of 99.99 percent. Furthermore, the specific operating conditions must be established under which the 99.99 percent DRE is achieved.

The development of a ranking of the incinerability for compounds which are candidates for POHC selection is of obvious utility. The US-EPA currently is using a ranking based on the heat of combustion per gram of pure compound (2). This method has received considerable criticism, and the development of an alternative ranking scheme is of a very high priority to the EPA.

Experimentally determined gas phase thermal stability under controlled laboratory conditions has been proposed as an alternative ranking method (3,4). Laboratory studies of the thermal decomposition of actual waste samples have been successful in predicting the most stable components of the waste and the formation of products of incomplete combustion (PICs) (5,6,7,). These direct comparisons of laboratory and full-scale results represent the only reported success of a proposed ranking scheme (8,9,10, 11, 12). These comparisons are included in Appendix D.

In this report we present the results of the laboratory determination of the gas phase thermal decomposition properties of twenty (20) hazardous organic compounds. The compounds were selected by EPA based on their frequency of occurrence in hazardous waste samples, apparent prevalence in the stack effluent, and representativeness of the spectrum of hazardous organic waste materials.

This portion of our program was concerned only with the relative thermal stabilities of these compounds in an oxidative atmosphere and did not include the measurement or determination of stable products of incomplete combustion. Thermal decomposition profiles were determined at various reactor residence times which enabled the calculation of global decomposition kinetic parameters. More detailed studies on mixtures and pure compounds under a variety of incineration conditions are in progress and will be reported separately.

The report includes a review of various proposed hazardous waste incinerability ranking procedures. The results of our laboratory measurements are then compared with these proposed ranking procedures. We have also attempted to correlate our data with various parameters which may relate to gas phase thermal stability. Finally, we provide a discussion of the mechanisms which may be responsible for the thermal decomposition of the twenty test compounds and how these mechanisms may be used to explain trends in the data and used to predict the relative thermal stability of untested compounds.

SECTION 2

CONCLUSIONS

- Based on data generated in this study of 20 test compounds and current understanding of chemical and physical phenomena occurring in an incinerator, laboratory determined gas phase thermal stability appears to be an effective means of ranking the destructibility of hazardous compounds in a waste. The relative thermal stability of certain organic compounds can be explained and possibly predicted using fundamentals of organic chemistry and kinetics if the full range of decomposition mechanisms is considered.
- Numerous products of incomplete combustion were formed during the thermal decomposition of a majority of the compounds. Many of these potential incineration products are of environmental impact and should be included in a complete assessment of the incinerability of a hazardous waste stream. Furthermore, identification of these products, which was not attempted because of time constraints, would be useful indicators of possible chemical reaction pathways.
- No single physical or chemical property of the test compounds is suitable as a ranking scheme for the entire list of 20 compounds.
- Compounds which are resistant to OH addition and whose weakest bond strength is large (>90 kcal/mole) will tend to be the most thermally stable.

- The range of temperatures required for 99.99% destruction efficiency for the 20 test compounds at two seconds mean residence time in flowing air is 600 to 950°C. There does exist a significant spread in the gas phase thermal stability of hazardous organic compounds.
- A pseudo-first order kinetic fit of the data is acceptable for describing the overall thermal decomposition behavior of the test compounds. Such modeling is necessary for extrapolation of the data to other conditions. More thorough kinetic and mechanistic studies are necessary before these kinetic parameters should be used as an indication of the elementary reaction mechanism.
- The great majority of existing fundamental reaction kinetic data from atmospheric chemistry and shock tube studies are inappropriate for the temperature range experienced in incineration.

SECTION 3

RECOMMENDATIONS

- Studies including more thorough kinetic investigations and identification of products of incomplete combustion should be conducted on a limited number of selected compounds for the purpose of identifying the dominant mechanisms of destruction of hazardous organic compounds as well as formation of toxic products of incomplete combustion.
- Any further survey studies of thermal stability of hazardous organic wastes should be conducted under what might be determined 'fault' modes of an incinerator as calculations indicate these modes control the incineration efficiency. A representative fault mode might be 1% oxygen (or less for other types of destruction systems than incinerators) and a residence time of 0.25 seconds. All data should be obtained in a standard organic test mixture spiked with the test compound or with a sample of an actual waste mixture to be subjected to incineration.
- Emphasis should be placed on the determination of the relative importance of various fault modes such as reduced gas phase residence time, low levels of oxygen, and low exposure temperature. This should combine laboratory measurements under carefully controlled conditions and scale up of this data using either theoretical distribution functions, or more ideally, distribution functions determined by actual field measurement. Such studies would actually address the effect of poor mixing (e.g., low oxygen concentration) on the molecular level.

- Studies should be performed to address the effect of changing the composition of the organic fraction of the reaction atmosphere since this has the potential of modifying the reaction pathway, thereby affecting thermal stability and product formation.
- A laboratory study designed to determine the rate of OH attack on hazardous organic compounds at incineration temperatures should be undertaken in light of the importance of this reaction inferred from this study. This should be conducted in concert with theoretical estimation or actual measurement of OH concentrations in full or pilot-scale systems.
- Organizations performing incineration research for the US-EPA should meet periodically in an informal workshop atmosphere to discuss new results and coordinate future research activities.
- A round-robin test program should be conducted on a complex waste sample to be subjected to incineration. The waste should be evaluated by each proposed incinerability ranking scheme and predictions made concerning the organic composition (both POHCs and PICs) of the stack effluent. The results of a trial burn of this waste at the US-EPA's Combustion Research Facility should be used as the basis for evaluation of the test program results.

SECTION 4

BACKGROUND

In this section we present a brief, general description of the processes occurring in incineration and the modes of thermal destruction of a hazardous organic waste. The concept of gas phase, thermal destruction and how it relates to the overall process of incineration is discussed.

INCINERATION PROCESSES

In determining the destruction efficiency of hazardous organic materials by incineration, we may effectively neglect chemical reactions occurring in condensed phases. This is true due to mass and heat transfer problems. Thus we may effectively concern ourselves only with gas-phase chemistry although the nature of the passage of material from condensed phase into the gas phase by physical processes may be important. However, once in the gas phase there exists more than one mode of destruction of the material and it is still necessary to address the factors affecting these destruction modes. Two modes are clearly evident and we may designate them as direct flame and thermal (nonflame).

The high temperature required to promote oxidation reactions may be generated from actual combustion of organic constituents of the waste or from cofired auxiliary fuel. The oxidizer may be the oxygen in the waste stream or outside makeup air. If combustion is carried to completion, a hazardous waste stream containing hydrocarbons will be converted to carbon dioxide (CO_2) and water (H_2O) while those wastes containing heteroatoms, such as atomic chlorine (Cl) will also form hydrochloric acid (HCl)

and molecular chlorine (Cl_2). Frequently, however, combustion is less than perfect and partially oxidized products of incomplete combustion may be formed. These may include carbon monoxide (CO), soot, and (most important) other organics which may be more hazardous than the parent compounds. It is always possible to overdesign an incinerator to ensure sufficiently complete destruction; however, this is usually done by building a very large incinerator and by using extra fuel for higher flame temperatures. Both of these are very costly.

The direct flame and thermal destruction modes are quite interrelated. As their names imply, the direct flame mode involves reaction and destruction within the flame itself, while for the thermal mode, the flame serves as a heat source for generation of very hot gases which in an oxidizing atmosphere promote destruction of organic materials.

Flames are gas-phase chemical reactions which may propagate through space as a result of fast chemical reaction and slower molecular transport. Flames are characterized by peak temperatures usually in excess of $1,000^\circ\text{C}$ (although lower temperatures are possible) and a radical rich atmosphere. This atmosphere consists primarily of atomic hydrogen (H), atomic oxygen (O), hydroxyl radical (OH), possibly methyl radical (CH_3) in carbon-hydrogen-oxygen systems, and additionally Cl and chloroxy radical (ClO) in chlorine-containing systems. There are usually several sequential reaction pathways with the reaction rate controlled by the slowest step in the fastest path.

The thermal zone of an incinerator surrounds and exists beyond the flame. This zone is characterized by temperatures between 650°C and $1,400^\circ\text{C}$ and a reaction atmosphere consisting of a mixture of nitrogen, oxygen, carbon dioxide, water, hydrogen chloride, chlorine, organic compounds, intermediates, and radicals. Although the reaction conditions are much less severe, the time spent by the materials subjected to incineration in the thermal zone is much greater than the time endured in the flame (a few seconds versus milliseconds).

A comprehensive model of an incinerator must take into account chemical reaction rates and mass and energy transport rates. Transport rates or chemical reaction rates may control the overall destruction rates under a given set of conditions. Chemical rates are important to determine temperature, residence times, and oxidizer concentrations needed to effectively destroy specific waste materials. Mixing times are important since they can affect the rates of destruction either by mixing of fuel, oxygen, reactive radicals, and intermediates with unreacted starting material.

Three characteristic times may be used to aid the characterization of the operation of an incinerator (13).

1. Mean Residence Time - The mean residence time is given by $\bar{t}_r = L/V$ where V is the average gas velocity and L is the length of the combustion zone. This is used to characterize the more important, and usually very different, residence time distribution.
2. Mixing Time - The mixing time is estimated by $t_d = L^2/D$ where D is the effective diffusion coefficient of the parent material.
3. Chemical Reaction Time - The reaction time for a first order, or pseudo first order, reaction is defined as $t_c = 1/k$ where k is the rate constant for the overall destruction reaction of the parent.

The relative magnitude of these numbers can give insight into what factors are controlling the rate of destruction. When t_c is small relative to t_d , then mixing is controlling and vice versa. When $\bar{t}_r$ is very small relative to t_c or t_d , poor destruction efficiencies are obtained by the incineration system. In general, these parameters are poorly understood as to how they relate to molecular processes. This has led to a considerable number of errors in discussions of operating efficiencies of incinerators.

There are many variations in the designs of contemporary industrial and municipal incineration systems. The major variations in design are necessary to accommodate the wide fluctuations in the characteristics of the various wastes. Other design variations have been introduced as incinerators have had to become more efficient and as better technology has been developed.

Almost all incineration systems use a refractory hearth to support burning waste or different types of grates which mix the solid waste during the combustion process. Suspension burning is the only process which does not necessarily require a hearth or grate, although a burnout grate is usually necessary at the floor of the furnace to catch the residue or incompletely combusted material.

While municipal incinerators are designed primarily to dispose of mixed municipal solid wastes, industrial or hazardous waste incinerators must be designed to handle solids, sludges, pasty materials, liquids, and gases. Industrial waste incineration systems are classified according to the nature of the waste, although it should be recognized that more than one type of waste is often burned in an adapted system. All basic incinerators must include a feed system, a refractory or protected metal enclosure, a waste support grate or hearth, a combustion air system, a solid residue withdraw system, and a flue gas exhaust system. Afterburners are almost always employed when the wastes are particularly dangerous and must be destroyed with high efficiency.

Let us consider what might be considered a typical hazardous waste incineration system as depicted in Figure 1. This system selected for examination consists of a rotary kiln followed by a secondary combustion chamber (afterburner) equipped for direct injection of liquid wastes. The rotary kiln would typically handle drums or cartons of solid waste and dewatered sludges. Liquid wastes are injected directly into the flame of the secondary combustion chamber. The effluent from the rotary kiln is admitted to the entrance of the secondary combustion

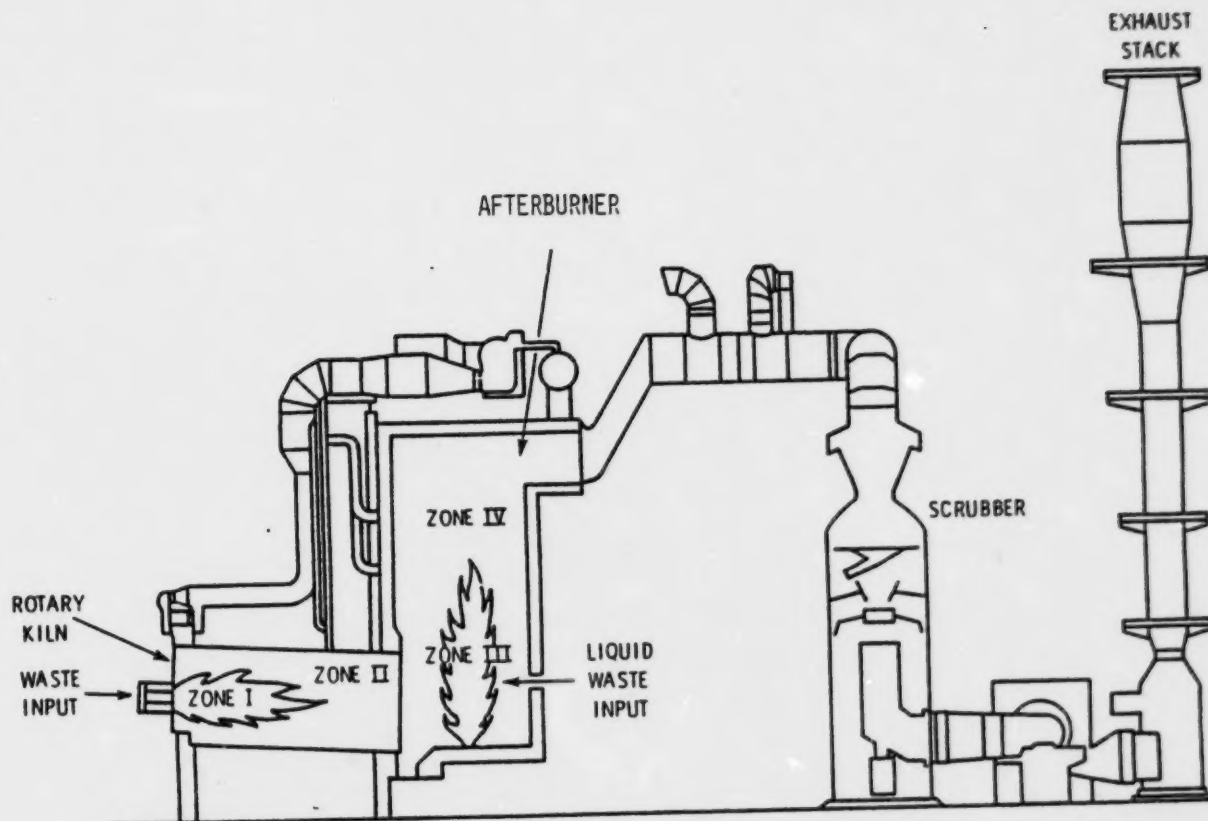


Figure 1. Simplified Diagram of an Incineration System Consisting of a Rotary Kiln and Secondary Combustion Chamber. The Four Destruction Zones Discussed in the Text are Labeled in the Figure.

chamber while the effluent from both the rotary kiln and the secondary flames is further degraded in the high-temperature oxidation region of the afterburner.

The overall incineration process can be divided into four destruction zones:

- I Rotary Kiln Flame Zone
- II Rotary Kiln Thermal Decomposition Zone
- III Afterburner Direct Flame Zone
- IV Thermal Oxidation Zone

Each of these zones may be discussed in terms of conditions encountered and processes occurring.

Rotary Kiln Conditions - Zones I and II

A rotary kiln is comprised of a cylindrical, refractory-lined steel shell. The kiln is sloped at less than 3 cm/m and is typically rotated at less than 2 rpm. The internal surface may be smooth or contain ridges which force materials to tumble. Sometimes baffles are used to improve contact between solids and combustion air flow which may be concurrent or countercurrent to solid flow. The speed of movement of the solid is controlled by speed of rotation of the kiln.

The waste is fed into the higher end of the kiln with a loading usually in the range of 3 to 12 percent of the cross-sectional area. The time/temperature profile depends upon whether the kiln is operating with concurrent or countercurrent flow. In concurrent flow, a large burner is used to heat the incoming waste. By the time an undewatered waste has been dried to the point where ignition can succeed, the waste may be too far from the burner for reliable ignition. In countercurrent flow, the burner is mounted at the discharge end and fires against the flow of waste. Wastes pass through the kiln gradually drying until they ignite and burn before exiting the kiln.

Typically, rotary kilns are designed to operate with bulk gas temperatures in the range of 700 to 1,000°C, depending upon the point in the kiln. Mean oxygen concentrations are in the range of 8 to 15 percent and mean residence times are about one second, although sizeable excursions from these mean values may occur during frequent upsets of the desired optimum operation.

Rotary Kiln Processes - Zones I and II

Numerous physical and chemical processes occur as solid waste is introduced into the kiln (see Figures 2 and 3). What possible pathways are available to the solid waste? With little hesitation we can assert that the material must enter the gas phase for destruction to occur to any extent. This may occur by sublimation, melting and vaporization, degradation, or pyrolysis (nonvolatile materials). If pyrolysis occurs, clearly the composition of the material subjected to gas-phase destruction may be very complex. Pyrolysis of the vapor may also occur before it has time to mix with make-up air and combustion gases. Again this leads to a complex mixture of species that is subjected to gas-phase destruction. Much of the vaporized waste will mix with air and undergo combustion. The flame mode of destruction basically involves attack by H, O, OH, and CH₃. In the process, many intermediates and radicals are generated which may initiate thermal reactions outside the flame zone. Although temperatures in the flame are typically greater than 1,000°C and the reaction pool is rich in reactive materials, the residence time in the flame is on the order of milliseconds and many mechanisms exist whereby organic materials can escape the flame environment.

Several factors which may affect the rate of waste destruction are:

- (a) rate of gasification;
- (b) rate of pyrolysis and product formation;
- (c) mixing of waste, fuel, and oxygen;
- (d) mixing of waste and reactive radicals and intermediates;

THERMAL DECOMPOSITION PROCESSES

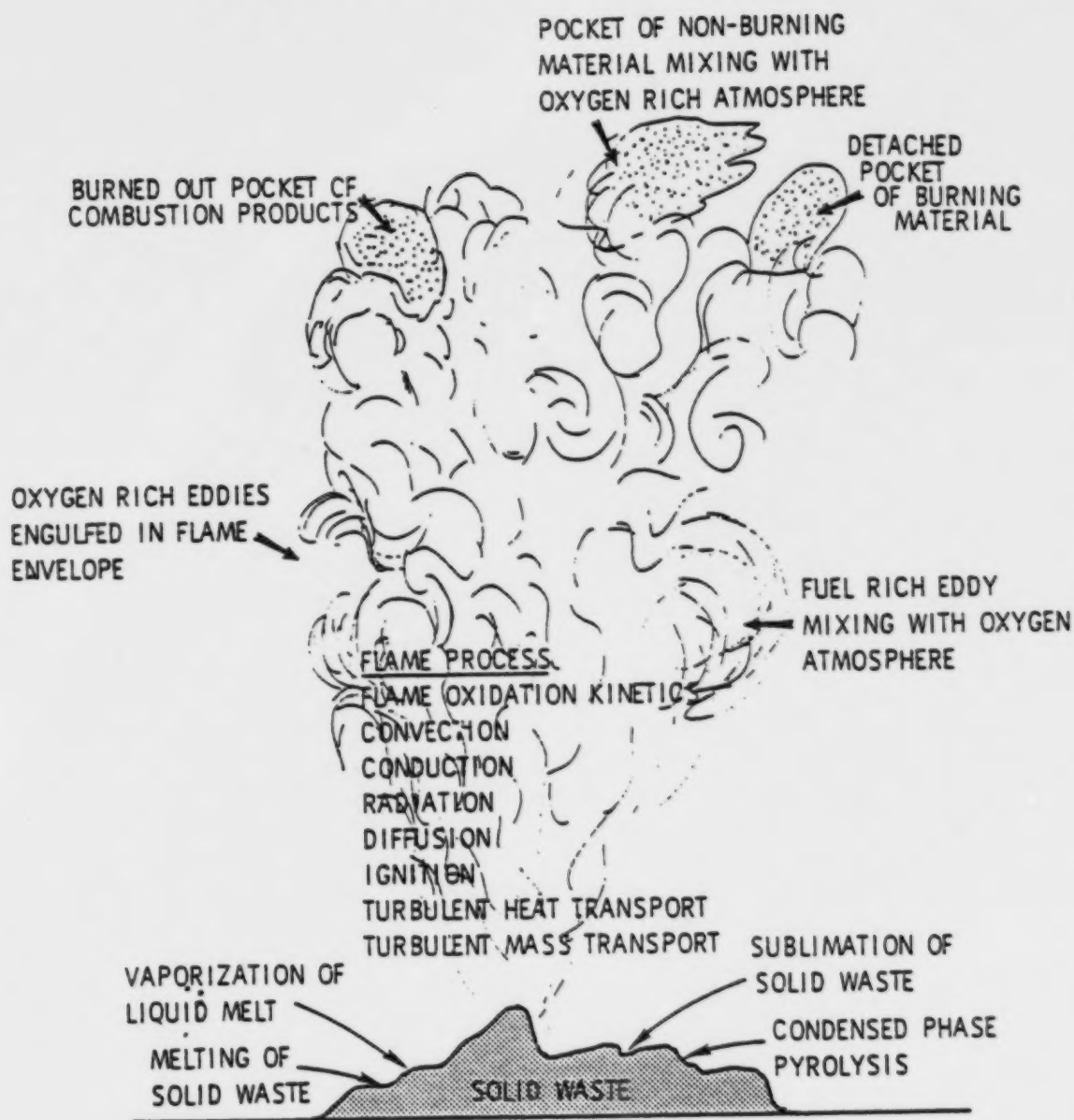


Figure 2.

Conceptual Depiction of Processes Occurring During the Destruction of a Solid Waste.

- (e) rate and products of thermal oxidation; and
- (f) rate and products of flame oxidation.

It should be noted that modes exist for the short circuiting of the cycle given in Figure 3. For example, pyrolyzed products may escape significant oxidation and pass through the kiln without further decomposition. Most notably, it has been observed in rotary kilns that as a large bulk of waste is fed into the system, it may flame up and use much of the available oxygen, thus subjecting the vaporized material to a pyrolyzing environment. It would then be necessary to deal with this effluent in the afterburner. A more detailed discussion of upset or fault modes of incinerator operation is included in the following subsection.

Afterburner Conditions - Zones III and IV

An afterburner is designed for two purposes: first, to handle the destruction of liquid wastes by direct injection into the combustion chamber, and second, to facilitate the complete destruction of partially destroyed material issuing from the rotary kiln. This is accomplished in two basic modes, direct flame degradation and thermal oxidation.

The destruction of liquid waste is aided greatly if the liquid is first atomized. This allows combustion air to rapidly engulf the resulting droplets to produce a combustible mixture. In addition, fine atomization increases the rate of vaporization of the waste which is a necessary prerequisite for ignition and combustion. For the purpose of our discussion, the method of atomization is relatively unimportant except for the size of the droplets produced. Contemporary, efficient atomization systems produce droplets with physical diameters in the range of a few microns to a few hundred microns.

The afterburner is typically a large rectangular or cylindrical refractory-lined chamber. The burner may typically be a longitudinal, axial, or vortex type. With each type of burner, waste alone may be burned if there is a high enough fuel content. Most

often this is not the case and supplementary fuel must be introduced. Typically, two or more separate or concentric nozzles are used to introduce fuel and waste. Combustion air may be introduced from the same nozzles as fuel and waste to aid in mixing.

In the axially fired afterburner, the flame originates at the upstream end of the chamber and fires down the centerline. This prevents flame impingement on the refractory and thereby reduces maintenance. However, poor mixing of fuel, waste, and oxidizer, plus very little recirculation occur, and this results in low residence times and poor reaction efficiency.

In the radially fired afterburner, the burner is located on either the axis or the side wall and fires along the radius. This represents an improvement over the axially fired system because of increased turbulence and mixing. However, flame lengths are shorter to prevent impingement on the refractory, thus reducing the direct flame residence time.

The vortex type burner represents a significant increase in combustion efficiency by using tangential or swirl entry designs. These designs allow longer flame lengths and increased mixing, thus optimizing combustion efficiency.

Mean total residence times in afterburners in waste incinerators may range from 1 to 12 seconds, although 2 to 4 seconds is most typical. The actual residence in the flame is in the range of 1 to 100 milliseconds. In our model incineration system, the exhaust gases from the kiln are mixed with the make-up air from the secondary combustion chamber. Fluctuation in combustion in the kiln and secondary chamber make the oxygen level in the chamber somewhat variable. Typically values may range from two to ten percent. Flame temperatures are well in excess of $1,000^{\circ}\text{C}$ while the bulk gas temperature in the chamber outside the flame may range from 600°C to $1,100^{\circ}\text{C}$.

It should be noted that the secondary combustion chamber in our model system has many of the general characteristics of

a fume afterburner. Off gases from the kiln are subjected to a short-duration, very high-temperature, reactive environment in the flame. Gases evolved from this secondary flame are then subjected to the high-temperature nonflame region of the system. In this region, high-temperature thermal decomposition of unreacted and partially reacted materials occur.

Afterburner Direct Flame and Thermal Oxidation Processes - Zones III and IV

The chemical and physical processes occurring in the afterburner chamber are quite similar in many respects to those occurring in the kiln. The most obvious difference is that we are no longer dealing with the solid state (except for solid particles escaping from the kiln and some very limited gas-to-aerosol conversion). Aspects of behavior of liquid fuel are depicted in Figure 4. Subprocesses occurring in the afterburner are the same as those observed in the kiln with the deletion of those subprocesses involving solids.

Although finite times for vaporization of the liquid droplets exist, it has been calculated that this time is negligible relative to the mixing and chemical reaction times for droplets less than 100 microns in diameter (14). New efficient nozzles are capable of producing aerosol distributions with droplets smaller than this; thus we may effectively neglect the vaporization phenomenon for liquid droplets. In the secondary combustion chamber we are addressing only the gas-phase oxidation rate of the waste materials and intermediate combustion products. Atomization efficiency may, however, be a problem when the nozzle is not operating properly and may be considered an upset mode of the system.

The modes of destruction in the direct flame zone and thermal oxidation zone are similar to those in the rotary kiln. The compositions of the reaction atmosphere are, of course, somewhat different as are the temperatures and residence times. The degree and nature of mixing may also be quite different due to the difference in configuration of the rotary kiln and secondary combustion chamber.

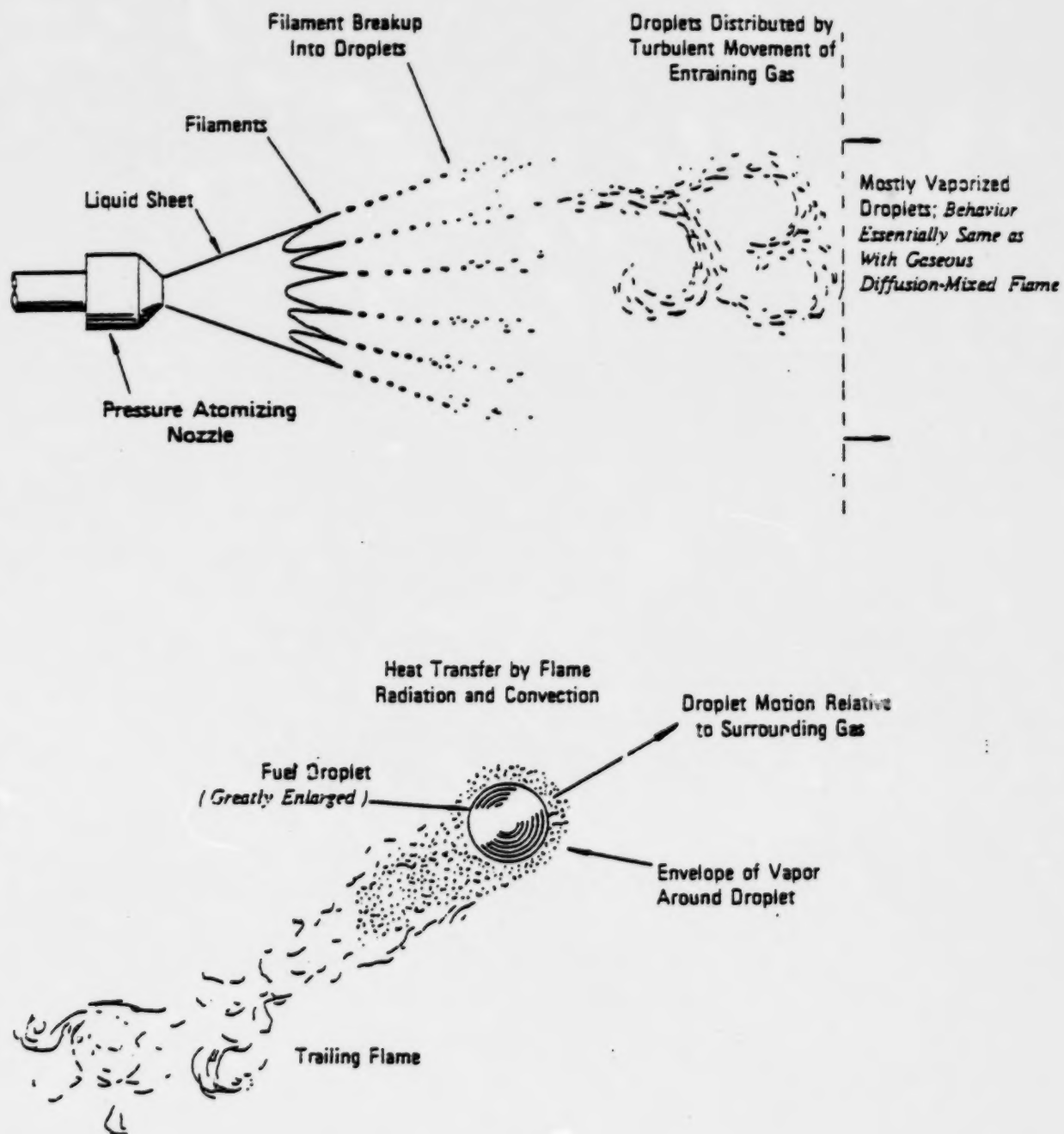


Figure 4. Diagram of Behavior of Liquid Wastes and Fuels.

The thermal oxidation zone of the afterburner is characterized by high temperatures and long residence times ($\sim 900^{\circ}\text{C}$ and 2 seconds) which are theoretically sufficient to destroy practically any gas-phase species subjected to this environment to a destruction efficiency of approximately 99.99 percent. This zone must effectively act as the 'killer' for all unreacted or partially reacted materials issuing from the previous zones in the incinerator. However, the very existence of measurable stack emissions indicates that there exist 'exceptional' molecules which escape the bulk conditions encountered in any of the four previously described zones. This has led to the concept of system upsets or fault modes of incineration.

SYSTEM UPSETS AND THEIR EFFECT ON FLAME AND THERMAL DECOMPOSITION

Both flame mode and thermal destruction studies indicate that any known organic waste can be destroyed to greater than 99.99% DE by either destruction mode alone if they are operating under theoretically optimum conditions. (14,15) Thermal destruction can be expected at less than $1,000^{\circ}\text{C}$ in flowing air at a mean residence time of 2.0 seconds. Flame destruction of waste droplets may be induced by flames operating in excess of 850°C . The fact that these theoretical optimum conditions roughly correspond to the mean conditions experienced in an incinerator has caused much confusion. The observation of organic emissions from incinerators (sometimes in large quantities) is proof that frequent excursions from the ideal, or mean, conditions are occurring.

These excursions, or fault modes, are probably the controlling phenomena for incineration efficiency. Flame studies have identified four upset parameters which affect flame mode destruction efficiency. (14) These are:

1. Atomization - Large droplets, produced by poorly designed or damaged nozzles, may penetrate the flame zone before ignition can occur.
2. Mixing - Poor turbulent mixing can result in poor contact of waste and oxygen on the molecular level.
3. Thermal - Flame temperatures may briefly drop due to high heat removal rates, quenching by mixing with excessive amounts of air, and low calorific value and uneven feed of waste material.
4. Quenching - Reactants may be quenched by mixing with cool gases or contact with a cool surface.

Laboratory studies have shown that relatively small excursions from ideality for these parameters can easily drop measured flame destruction efficiencies from greater than 99.99% to 99% or even less than 90% (three orders of magnitude).

Non-flame upset parameters can also be classified. We prefer to discuss these parameters in terms of continuous distributions. (6,15)

1. Oxygen Distributions - Poor mixing can result in some molecules seeing molecular oxygen levels on the order of 1% or even less.
2. Residence Time Distribution - Turbulent mixing in the chamber and entrainment of material in the high velocity flame front can result in very short residence times. Poor atomization or waste sealed in particulate matter may reduce gas phase residence times to well less than a quarter of a second.
3. Temperature Distribution - Cool walls and quenching by makeup air can result in significantly reduced temperature for portions of the gas volume.

The key to understanding the significance of upset conditions is that only a very small fraction of the total volume of the waste need to experience these less than optimum conditions

to result in significant deviations from the targeted destruction efficiencies. The poor destruction efficiency of this small fraction effectively controls the overall destruction efficiency for the entire waste volume.

Scientists and engineers have been working on optimizing flame combustion for at least 75 years in conjunction with internal combustion and jet engine research. Even at its highly developed level, non-flame, high temperature long residence time thermal oxidation zones have been and still are necessary for an incinerator to operate efficiently.

Based on laboratory investigations, field studies, and engineering design, we can expect modern, well-designed incinerators to typically achieve 99% DE in the flame zone. This means that the one percent of the material which escapes the flame through some fault mode must be dealt with effectively and destroyed to an additional 99 percent in the thermal oxidation zone for the incinerator to achieve the desired overall level of 99.99 percent destruction. Furthermore, the mode of destruction designated "flame" mode is actually a high temperature gas phase thermal oxidation and has much in common with non-flame processes. Since all material experiencing optimum flame conditions would be totally destroyed, then the escaping material must have experienced either a shorter residence time or less severe reaction atmosphere similar to that of a non-flame environment. Thus, the majority of the material comprising the incinerator effluent may well be composed of species produced in a non-flame thermal oxidizing environment.

This apparent influence of high temperature, gas phase thermal oxidation on the process of incineration has stimulated our approach to research in this area. In the sections that follow, we respectfully submit our research findings to the existing body of scientific data on incineration.

SECTION 5

EXPERIMENTAL PROCEDURES

All of the experimental data presented in this report was generated on the thermal decomposition unit-gas chromatographic (TDU-GC) system which was designed and built with funding provided by the US-EPA (Cooperative Agreement No. 807815-01-0). Samples of the 20 compounds were prepared and introduced to the system by several procedures depending upon their physical state and vapor pressure. Sample source and handling information is included in Table 1. A description of the TDU-GC and the sample handling procedures are presented in the following paragraphs.

INSTRUMENTATION

A block diagram of the TDU-GC system is given in Figure 5 and an artist's rendering of the system is given in Figure 6. As seen in Figure 5, the TDU-GC system is a closed, in-line system. Using compressed gases, the analysis atmosphere can be chosen (i.e., 100% O₂, air, nitrogen, etc.). In addition, in-stream instrumentation, described later, provide accurate measurement of pressure and flow. Most of the TDU-GC system's instrumentation controls are located in a console from which test functions can be continuously monitored.

A simplified account of the events taking place in the TDU-GC system is as follows. The sample is introduced into the system and gradually vaporized in a flowing gas stream (i.e., nitrogen, air, or nitrogen/oxygen mixtures). The vaporized sample passes through a controlled, high-temperature tubular reactor where it undergoes thermal decomposition. The products evolving from the thermal decomposition of the compound and the remaining parent compound are swept into a Varian VISTA 4600 high-resolution gas chromatograph (HRGC)

TABLE 1

SAMPLE HANDLING AND SOURCE INFORMATION

<u>Name</u>	<u>Source</u>	<u>Purity</u>	<u>M.P.</u> <u>(°C)</u>	<u>B.P.</u> <u>(°C)</u> 760mm	<u>Method of</u> <u>Insertion</u>
Acetonitrile	Manufacturing Chemistry Inc.	99%	-45.72	81.6	Premixed Gas
Acrylonitrile	Aldrich Chemical Co.	>99%	-82	79	Premixed Gas
Aniline	Fisher Scientific Co.	A.C.S. 99%	-6.3	184.13	Premixed Gas
Benzene	Ultra-Scientific Corp.	>98%	5.5	80.1	Premixed Gas
Carbon Tetrachloride	Fisher Scientific Co.	A.C.S. 99%	-22.99	76.54	Premixed Gas
Chloroform	Fisher Scientific Co.	99%	-63.5	61.7	Premixed Gas
1,2-Dichlorobenzene	Ultra-Scientific Corp.	>98%	-17	180.5	Pure Liquid
Ethane	Matheson	>99%	-183.3	-164	Premixed Gas
Hexachlorobenzene	Ultra-Scientific Corp.	>98%	230	322	Cyclohexane Soln.
Hexachlorobutadiene	Ultra-Scientific Corp.	99%	-21	215	Cyclohexane Soln.
Hexachloroethane	Ultra-Scientific Corp.	99%	190-195 (subl)	186 ²⁹⁷ mm	Cyclohexane Soln.
Methane	Matheson	99%	-182.48	-88.63	Premixed Gas
Methylene Chloride	Fisher Scientific Co.	99%	-95.1	40	Premixed Gas
Monochlorobenzene	Ultra-Scientific Corp.	>98%	-45.6	132	Premixed Gas
Nitrobenzene	Fisher Scientific Co.	99%	5.7	210.8	Premixed Gas
Pyridine	Aldrich Chemical Co.	>99%	-42	115.5	Premixed Gas
1,2,3,4-Tetrachlorobenzene	Ultra-Scientific Corp.	>98%	54.5	246	Solid
Tetrachloroethylene	Aldrich Chemical Co.	99%	-19	121	Premixed Gas
1,2,4-Trichlorobenzene	Ultra-Scientific Corp.	>98%	16.95	213.5	Cyclohexane Soln.
1,1,1-Trichloroethane	Aldrich Chemical Co.	99%	-30.41	74.0-76.0	Premixed Gas

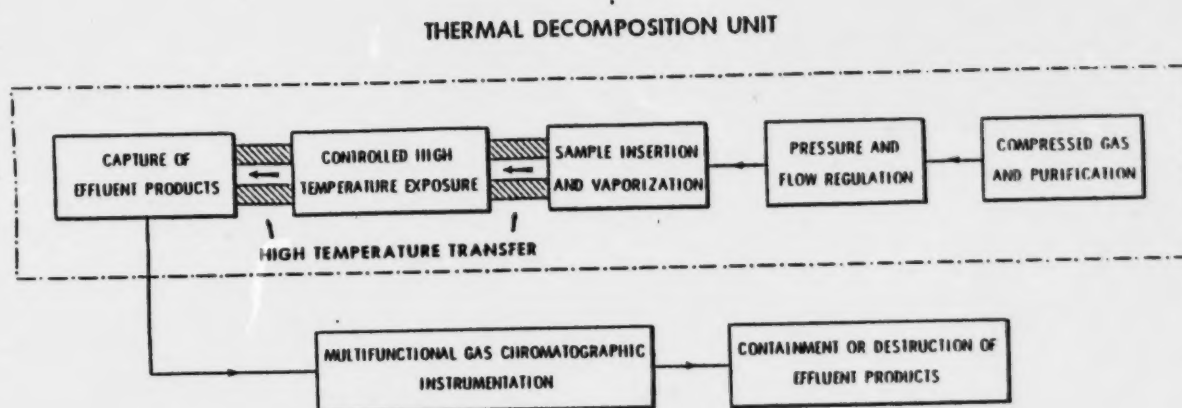


Figure 5. Block Diagram of the Thermal Decomposition Unit-Gas Chromatographic System.

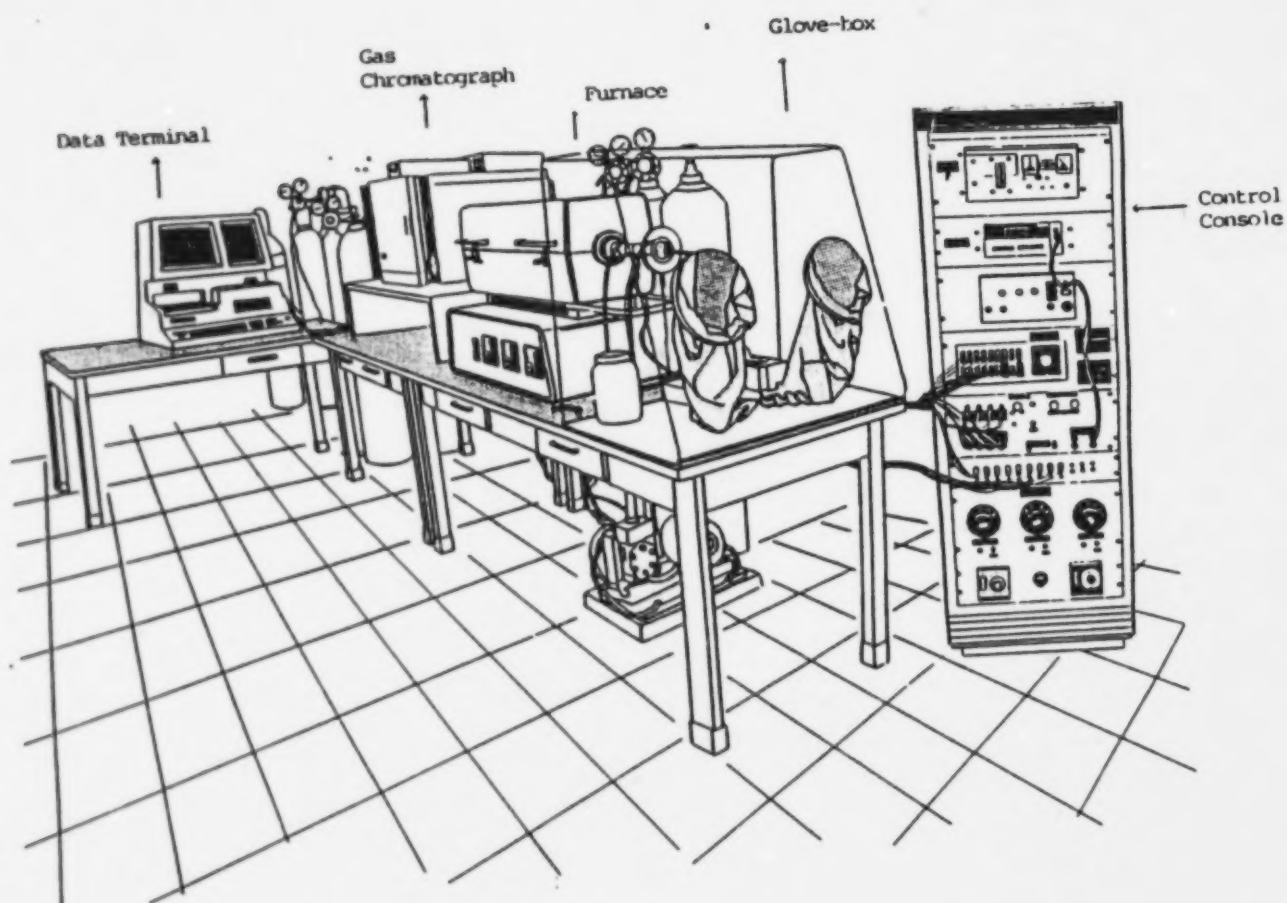


Figure 6. Thermal Decomposition Unit-Gas Chromatographic System

for analysis. The sample insertion chamber, the reactor, and the entire transport system are fabricated of fused quartz to minimize interaction with the sample. In the following sections, a detailed description of the TDU-GC system's components is given.

Sample Insertion

The rate at which molecules are admitted into the high-temperature reactor is an important factor in thermal decomposition studies. In the TDU-GC system, the sample is deposited into a sample insertion chamber which is packed with glass wool. The chamber is initially kept at room temperature or below. The chamber is slowly heated to 250-300°C by applying a linear temperature program (10°C-20°C/min). The sample molecules are gradually transported downstream into the thermal reactor.

The sample insertion section of the TDU-GC system is contained in a plexiglass glove box. The inlet of the fused quartz tubular reactor assembly is connected to a 1 mm ID quartz tube to which the sample insertion chamber is attached. The chamber accommodates a sample insertion probe. This probe consists of a fused quartz tube that allows the insertion of a chromatograph syringe needle through a septum receptacle on one end. A schematic of this probe is given in Figure 7.

The insertion probe has on the other end a cavity with slits in the wall for transport gas access and filled with loosely packed quartz wool. The quartz wool packing serves two purposes. The sample is deposited into the quartz wool at room temperature, as mentioned before, and may be temporarily retained until heat is applied. In addition, the quartz wool serves to wipe the syringe needle clean of any remaining sample as the syringe is removed from the injection probe. The 1.0 mm ID tubing which connects the insertion chamber to the reactor is surrounded by an outer quartz tube jacket. There are a number of heating elements located on the outer diameter of the entire insertion assembly which are controlled by a temperature programmer (Theall Engineering TP-2000) located in the instrumentation console. Using a flow of heat transfer air, a uniform temperature distribution is obtained for transporting the gas-phase sample from the insertion point to the reactor assembly.

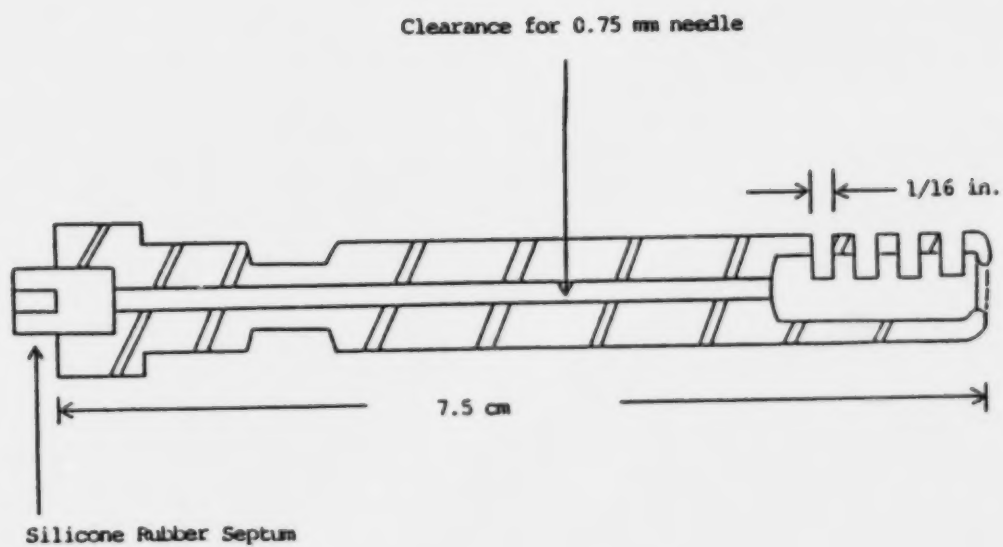


Figure 7. Cross-Sectional View of the TDU-GC's Sample Insertion Probe.

A Hamilton #7000.5 microsyringe was used for the liquid sample injections (0.5 μ l full travel). A Pressure Lok gas tight syringe (Precision Sampling Corp. - 100 μ l full capacity) was used to inject gas samples.

Quartz Tube Reactor

One of the most important components of the TDU-GC system is the high-temperature reactor. Design considerations for the reactor are found in a previous report on the development of the TDAS. [16] The major portion of the reactor consists of a narrow-bore nominal 1 mm ID quartz tube flow path in a race-track configuration (3.5 cycles, 1 meter in length). Quartz tubing was obtained from Heraeus-Amersil, Inc. The racetrack construction minimizes the possibility of wall reactions while simultaneously providing a very narrow residence time distribution and square wave exposure temperature profile. Details of the quartz tube reactor are given in Figure 8. In addition, the reactor design has very fine bore entrance and exit tubes to transport the sample rapidly into and out of the central portion of the reactor. This design also minimizes non-ideal temperature profiles. Tubing diameter measurements were obtained by the mercury displacement technique.

The multiple fold design in the race track reactor assures that sample molecules encounter essentially isothermal conditions during their traverse through the reactor due to the averaging of longitudinal temperature gradients. In addition, there is a very low pressure drop across the reactor even at high linear gas velocities (~ 0.145 atm at $1.0 \text{ sec } \bar{t}_r$). The average residence time of molecules that have passed through the reactor can be accurately determined.

The quartz tube reactor assembly fits into a high-temperature three zone Lindberg furnace of hinged construction (Model 54257).

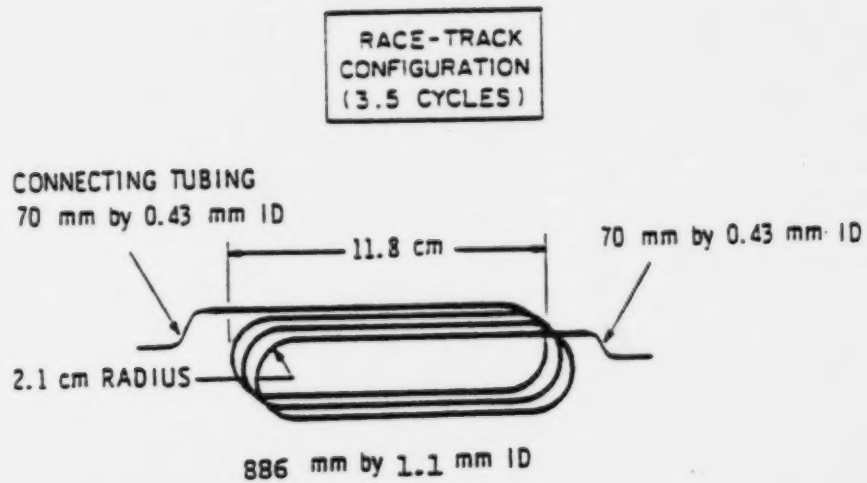


Figure 8. Detail of Quartz Tube Reactor.

This furnace is designed for continuous operation at temperatures up to 1,200°C, and the three zones are heated independently. The middle zone is used to heat the race track section of the reactor assembly. Figure 9 shows a cross sectional view of the furnace interior. The quartz tube reactor can withstand elevated temperatures for extended periods of time, and the furnace control console can maintain the temperature in a given zone of the furnace to $\pm 1^\circ\text{C}$.

There are three main gas flows in the TDU-GC system. The gas flow through the reactor carries the vaporized sample from the inlet assembly through the reactor's high-temperature zone. The undecomposed parent compound, along with any products of incomplete combustion (PICs), are swept downstream towards the HRGC where the sample is trapped cryogenically within the first few centimeters of the GC column (essentially the same as on-column injection) and subsequently analyzed.

The other two gas flow paths consist of independently adjustable flows of heat transfer air which cool the entrance and exit chambers of the quartz tube assembly. These chambers are located in Zones 1 and 3 of the high-temperature furnace. The effect of a sudden rise in temperature along the axial length at the entrance of the quartz tube reactor assembly, followed by a sudden drop in temperature at the exit produces a square wave thermal pulse which assures that the sample experiences the desired temperature for the calculated average residence times.

Sample Collection

The effluent from the high-temperature reactor zone, containing the remaining parent compound and the various decomposition products, is swept through a heated transfer line towards a gas chromatograph. Before reaching the inlet of the capillary column, a 30 to 1 split is effected and only a small portion ($\sim 3\%$) of the effluent sample enters the GC column. The larger portion of the sample is passed onto an activated charcoal trap which is vented to the atmosphere.

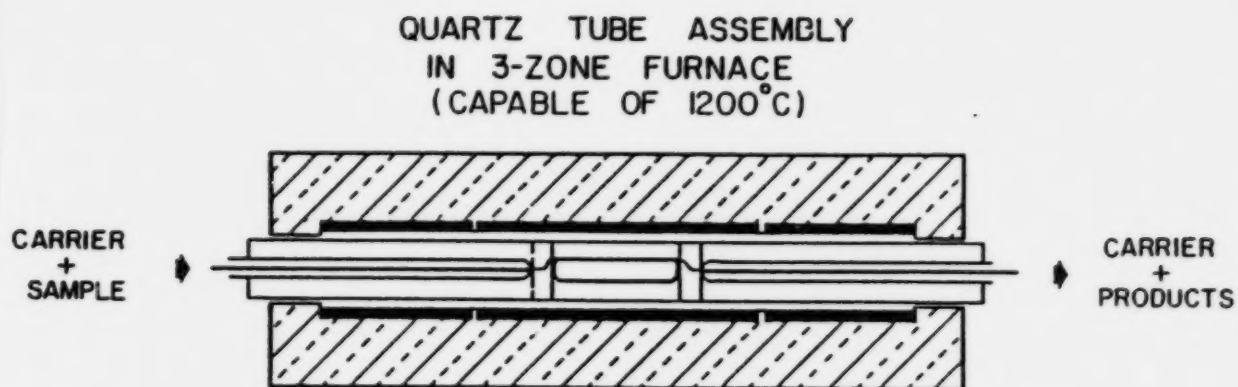


Figure 9. Cross-Sectional View of the TDU-GC Furnace Assembly.

Gas Chromatograph System

The TDU-GC system incorporates an in-line Varian 4600 Gas Chromatograph with a dedicated data terminal (VISTA CDS 401). All GC functions are controlled from the 401 terminal. The Varian HRGC is capable of generating a wide variety of temperature programs designed for continuous and unattended operation. The data terminal is capable of handling and reducing data from previous analyses while still another analysis is in progress. All samples except ethane were analyzed using this system.

The temperature in the GC oven can be maintained sub-ambient for any length of time through the use of a solenoid-actuated liquid nitrogen reserve that is connected to the GC instrument. A fused silica capillary column was used in the majority of the investigations (J & W Scientific, Inc.). The column was 15 meters in length and contained a chemically bonded dimethylsilicone stationary phase.

The sample emerging from the reactor was trapped at the head of the chromatographic column by maintaining the GC oven at a cryogenic temperature ($\sim$ minus 30°C). The SE-30 column can quantitatively capture, even at room temperature, most substances having a molecular weight of 100 or greater. Much greater resolution and sensitivity can be attained with a capillary column than with a conventional packed column. Other columns may be used for analyses of lower molecular weight species. The Varian VISTA 4600 can accommodate a number of detectors which, if desired, can be used simultaneously. A flame ionization detector was used in this investigation. The air flow was kept at $300\text{ cm}^3/\text{min}$ while the hydrogen flow was maintained at 270°C . Throughout the investigation the signal/noise ratio for peak detection was 4. (16)

For ethane analysis, Tedlar bags were used to capture the reactor effluent at the splitter. The captured gas was subjected to analysis in a Varian Aerograph Series 1800 gas chromatograph equipped with a one meter x 4.0 mm ID packed column (5 Å molecular sieve, 45/60 mesh) operated isothermally at 150°C .

Monitoring Instrumentation

The TDU system has a versatile and updatable instrumentation console which is used to monitor and control many of the experimental parameters, such as reactor temperature, flow rate, and pressure. A Cabtron Series C modular electronic cabinet was used as the basic frame for this console. The readout device for the pressure and mass flow transducer is represented in volts DC, while the output from the differential pressure transducer is displayed in millivolts DC. The temperature at various locations throughout the TDU-GC system is measured with the use of 18 different Chromel-Alumel thermocouples, a thermocouple selector switch (Omega MTG-OSW3-18), a digital temperature thermometer, and a less sensitive digital temperature indicator (Omega Model 22091). The temperatures of the three furnace zones, the various heated transfer lines, and the inlet assembly can be continuously monitored from the instrumentation console.

The gas flow control module consists of the gas input connectors, a carrier gas filter (Applied Science Laboratory), a gas switching valve (Carle Instruments #5511), needle valves to control the flow of heat transfer air in the high-temperature reactor assembly, a precise variable gas flow control valve (Porter Instrument VCD 1000), and the mass flow and pressure transducers along with their associated electronics. The mass flow transducer was calibrated to allow flow rates of up to $50 \text{ cm}^3 \text{ min}^{-1}$, while the differential pressure transducer was designed for use up to 2.0 absolute atmospheres.

Calibrations were done using the methods described in Appendix D of the TDAS design report.

SAMPLE PREPARATION AND HANDLING

Sample handling and preparation was performed in the TDU-GC system's glove-box compartment. Sample preparation was an important factor because of two reasons. First of all, the sample had to be sufficiently small so that oxygen would be in excess at all times to prevent pyrolysis. Secondly, due to delivery

restrictions in commercially available chromatographic syringes, injection size could not be smaller than 0.01 μ l to ensure good repeatability.

Samples of each compound studied were prepared according to individual characteristics. High vapor pressure liquid phase samples were prepared at concentrations of approximately 10 ppm (v/v) in air. (Precise quantitation is not required since data reduction employs a difference method involving the comparison of the partially decomposed sample peak size with a non-decomposed quantitation peak.) These samples were slowly injected onto quartz wool in a temperature programmable insertion chamber.

As an example of this procedure, benzene was analyzed as a gas in a closed Pyrex bulb fitted with a septum receptacle designed to minimize sample loss due to adsorption sites. Into the bulb, 30 μ l of benzene were introduced and allowed to evaporate. Using a Pressure Lok gas-tight syringe (Precision Sampling Corp. - 100 μ l full capacity), 50 μ l aliquots ($\sim$ 2 μ g benzene) from the sampling bulb were injected into the TDU-GC system. Quantitation analyses were performed periodically throughout the experiments.

Use of solvents was avoided, whenever possible, to facilitate PIC observation. However, for those samples run in solution, Eastman Spectra ACS Grade cyclohexane was selected as the solvent. Cyclohexane was chosen for its low thermal stability and high volatility relative to the specific solutes except for the case of 1,2,3,4-tetrachlorobenzene, for which sample was prepared in a methylene chloride solution. With the sample probe removed from the insertion chamber, the solution was injected into the quartz wool portion of the probe, the solvent was evaporated, and then the probe with the deposited tetrachlorobenzene was returned to the insertion chamber.

Individual solutions of monochlorobenzene (0.001 M) and hexachlorobenzene (0.022 M) in cyclohexane inserted into a glass wool probe where used to determine their thermal decomposition rates. The other chlorinated benzenes in this study were run as pure liquids, with 0.025 μ l of pure compound being injected onto a quartz wool probe.

All samples were stored in microvials with septa-lined caps in a refrigerator at 0°C. Weight determinations were performed on a Mettler Model H20 analytical microbalance.

SECTION 6

RESULTS

A series of twenty (20) hazardous organic compounds were subjected to laboratory thermal decomposition analysis using the TDU-GC. For each compound, the fraction of the feed material undestroyed at a given set of temperatures and mean reactor residence times ($\bar{t}_r$) were determined. This resulted in the generation of what may be termed thermal decomposition profiles, i.e., a logarithmic plot of weight percent remaining vs. the reactor temperature ($^{\circ}\text{C}$) at constant residence time. For each compound, thermal decomposition profiles were generated in flowing air at four mean residence times, $\bar{t}_r = 1.0, 2.0, 4.0$, and 6.0 seconds. An example of the determination of this family of profiles is given in Figure 10 for chloroform. The thermal decomposition profile for chloroform is representative of the great majority of the compounds tested and serves to illustrate several features.

Below 400°C , no measurable decomposition occurs, resulting in the flat portion of the curve. Between 400°C and 525°C the rate of decomposition begins to increase. Above 550°C , the rate of decomposition increases rapidly resulting in an apparently linear region of very large slope. The chloroform has been destroyed with 99.99% efficiency by 620°C at a residence time of 2.0 seconds.

The family of thermal decomposition profiles for each of the 20 compounds are presented in Appendix A. Each of these profiles exhibits essentially the same features as that for chloroform, the apparent differences in thermal stability being expressed through the temperature for onset of decomposition

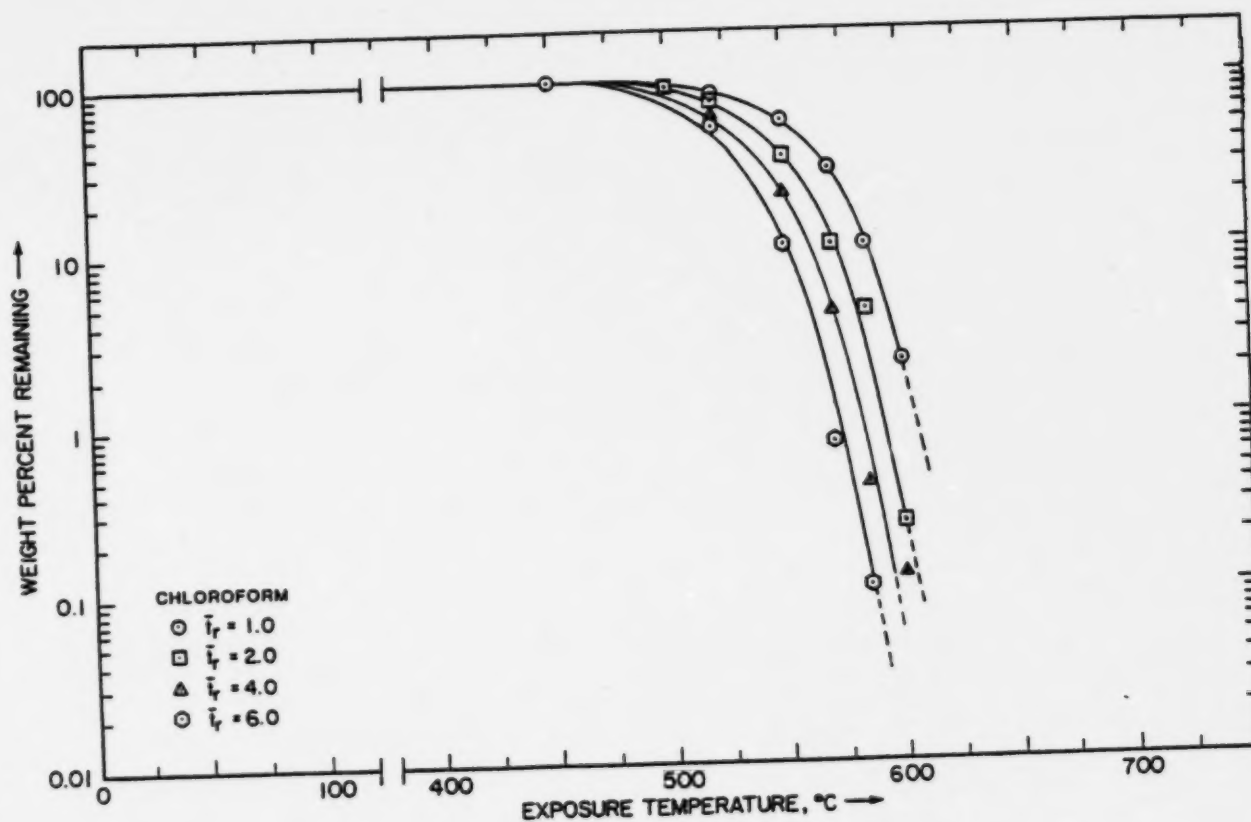


Figure 10. Thermal Decomposition Profiles for Chloroform in Flowing Air at Mean Residence Times of 1.0, 2.0, 4.0, and 6.0 Seconds.

and the slope of the fast decomposition region. This data has been summarized in Table 2 with entries for the temperature for the onset of decomposition, $T_{\text{onset}}(2)(^{\circ}\text{C})$, the interpolated temperature for 99% destruction $T_{99}(2)(^{\circ}\text{C})$, and the extrapolated temperature for 99.99% destruction, $T_{99.99}(2)(^{\circ}\text{C})$. All these values are for $\bar{t}_r = 2.0$ seconds in flowing air. Using only the data presented in this table, the thermal decomposition profile for each compound may be approximately reconstructed. The table lists the compounds in order of decreasing temperature required for 99% destruction efficiency. A slight reordering occurs if $T_{99.99}(2)$ is used for the ranking. However, the numerical differences for the reordered compounds are small.

FIRST ORDER GLOBAL THERMAL DECOMPOSITION KINETICS

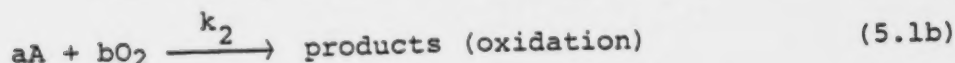
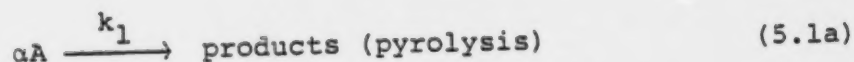
Mechanisms can be investigated at three levels: the overall or global reaction scheme, the elementary reaction scheme, and the chemical dynamic reaction scheme. Our work has succeeded in gaining a moderate understanding of some of the global reaction schemes involved in gas-phase thermal decomposition of compounds typically qualifying as hazardous wastes. Through fundamental studies by other researchers on very simple molecules and systems, we have some knowledge of the elementary reactions which may affect thermal decomposition in waste incinerators. Very little research has been conducted concerning the chemical dynamics of hazardous waste thermal decomposition.

For the conditions possibly encountered during gas-phase thermal decomposition in an incinerator (600°C to $1,400^{\circ}\text{C}$ and oxygen levels of 0.1 to 21 percent), two possible global pathways predominate. The first is pyrolysis, for which the rate of decomposition of the parent species is independent of the oxygen concentration. The second is oxidation for which the decomposition of the parent is dependent both on the oxygen concentration and susceptibility of the parent species to attack by oxygen or oxygen containing species.

The global expressions for these two reaction schemes are:

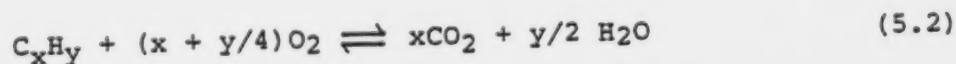
TABLE 2
SUMMARY OF THERMAL DECOMPOSITION DATA

<u>Compound</u>	<u>Empirical Formula</u>	<u>T_{onset} (2) (°C)</u>	<u>T₉₉ (2) (°C)</u>	<u>T_{99.99} (2) (°C)</u>
Acetonitrile	C ₂ H ₃ N	760	900	~950
Tetrachloroethylene	C ₂ Cl ₄	660	850	920
Acrylonitrile	C ₃ H ₃ N	650	830	860
Methane	CH ₄	660	830	870
Hexachlorobenzene	C ₆ Cl ₆	650	820	880
1,2,3,4-Tetrachlorobenzene	C ₆ H ₂ Cl ₄	660	800	850
Pyridine	C ₅ H ₅ N	620	770	840
Dichloromethane	CH ₂ Cl ₂	650	770	780
Carbon Tetrachloride	CCl ₄	600	750	820
Hexachlorobutadiene	C ₄ Cl ₆	620	750	780
1,2,4-Trichlorobenzene	C ₆ H ₃ Cl ₃	640	750	790
1,2-Dichlorobenzene	C ₆ H ₄ Cl ₂	630	740	780
Ethane	C ₂ H ₆	500	735	735
Benzene	C ₆ H ₆	630	730	760
Aniline	C ₆ H ₇ N	620	730	750
Monochlorobenzene	C ₆ H ₅ Cl	540	710	780
Nitrobenzene	C ₆ H ₅ NO ₂	570	670	700
Hexachloroethane	C ₂ Cl ₆	470	600	640
Chloroform	CHCl ₃	410	590	620
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	390	570	600

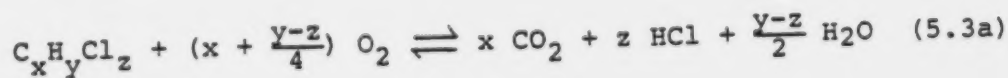


where: A is the concentration of the hazardous compound,
 O_2 is the oxygen concentration,
 α , a, and b are the stoichiometric coefficients for the global reactions, and
 k_1 and k_2 are the global rate constants for pyrolysis and oxidation, respectively.

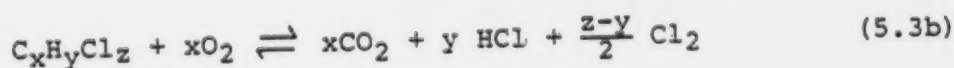
For years, hydrocarbons (primarily aliphatic) have been of intense interest to kinetic researchers due to their heating value and their role in the combustion process. In our research we have extended this work to include aromatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons, and heteroatomics classified as hazardous wastes. Complete hydrocarbon oxidation reactions may be represented by the chemical equation:



where C_xH_y is the general formula for any hydrocarbon. The oxidation of a chlorinated hydrocarbon may be represented by the chemical equation:



when $y > z$ or



when $y < z$. The inclusion of chlorine into the system introduces additional complexities into the analysis of the system not only for product formation but also from possible reaction pathways. This point will be discussed later.

Equation 5.1a and 5.1b lead to the general expression for the rate of disappearance of the parent

$$-\frac{d[A]}{dt} = k_1[A]^a + k_2[A]^a[O_2]^b. \quad (5.4)$$

The time dependence is included in this expression. The temperature dependence is included in the rate constants for the two processes. This may be expressed by the Arrhenius equation:

$$k = A \exp (-E_a/RT) \quad (5.5)$$

where: E_a is the activation energy for the process, cal mole⁻¹
 A is the Arrhenius coefficient, s⁻¹
 R is the universal gas constant, 1.99 cal mole⁻¹ °K⁻¹.

Our studies indicate that when the thermal decomposition reaction occurs in an atmosphere with a large excess of molecular oxygen, relative to the concentration of the waste material, the decomposition equation 5.4 may be simplified to an expression that is first order in the concentration of the waste:

$$-\frac{d[A]}{dt} = k_2' [A]. \quad (5.6)$$

In this expression the contribution of pyrolysis has been neglected, and the oxygen concentration which is nearly constant during the course of reaction has been included in the new pseudo-first order rate constant k_2' . This expression may be integrated to yield the familiar first order rate expression

$$f_r = \exp(-k_2' \bar{t}_r) \quad (5.7)$$

where: f_r is the fraction of the parent species remaining,
and
 $\bar{t}_r$ is the mean residence time in the reaction zone.

This expression may be combined with the Arrhenius Equation 5.5 to yield an expression for the required temperature for a given level of destruction.

$$T_{DE} = 503 E_a \left[\ln \left(\frac{-\bar{t}_r A}{\ln f_r} \right) \right]^{-1} \quad (5.8)$$

where: T_{DE} is the temperature required for a given DE, °K,
 E_a is the measured activation energy, kcal mole⁻¹,
 A is the measured Arrhenius coefficient, s⁻¹,
 $\bar{t}_r$ is the mean reactor residence time, s, and
 f_r is the fraction of the parent species undestroyed.

This expression may be generalized for any oxygen concentration as given by equation 5.9.

$$T_{DE} = 503 E_a \left[\ln \left(\frac{-\bar{t}_r A}{\ln f_r} \right) \left(\frac{[O_2]}{.21} \right)^b \right]^{-1} \quad (5.9)$$

where: $[O_2]$ is the fraction of oxygen in the reaction atmosphere,
 b is the order of the reaction with respect to oxygen as defined in Equation 5.4.

Following Equation 5.7, a plot of $\ln f_r$ vs. $\bar{t}_r$ for the four residence times will yield the rate constant for the reaction at a given temperature. A plot $\ln k$ vs. $1/T$ for the four experimental temperatures should then yield a straight line with the slope equal to $-E_a/R$ and an intercept of $\ln A$.

Regression analyses of this type have been performed on each of the twenty (20) test compounds. An example of the kinetic and Arrhenius plots for chloroform are given in Figures 11 and 12 respectively and the kinetic data sheets used to report the data is also presented in Table 3. The data sheets and kinetic plots for each of the test compounds are

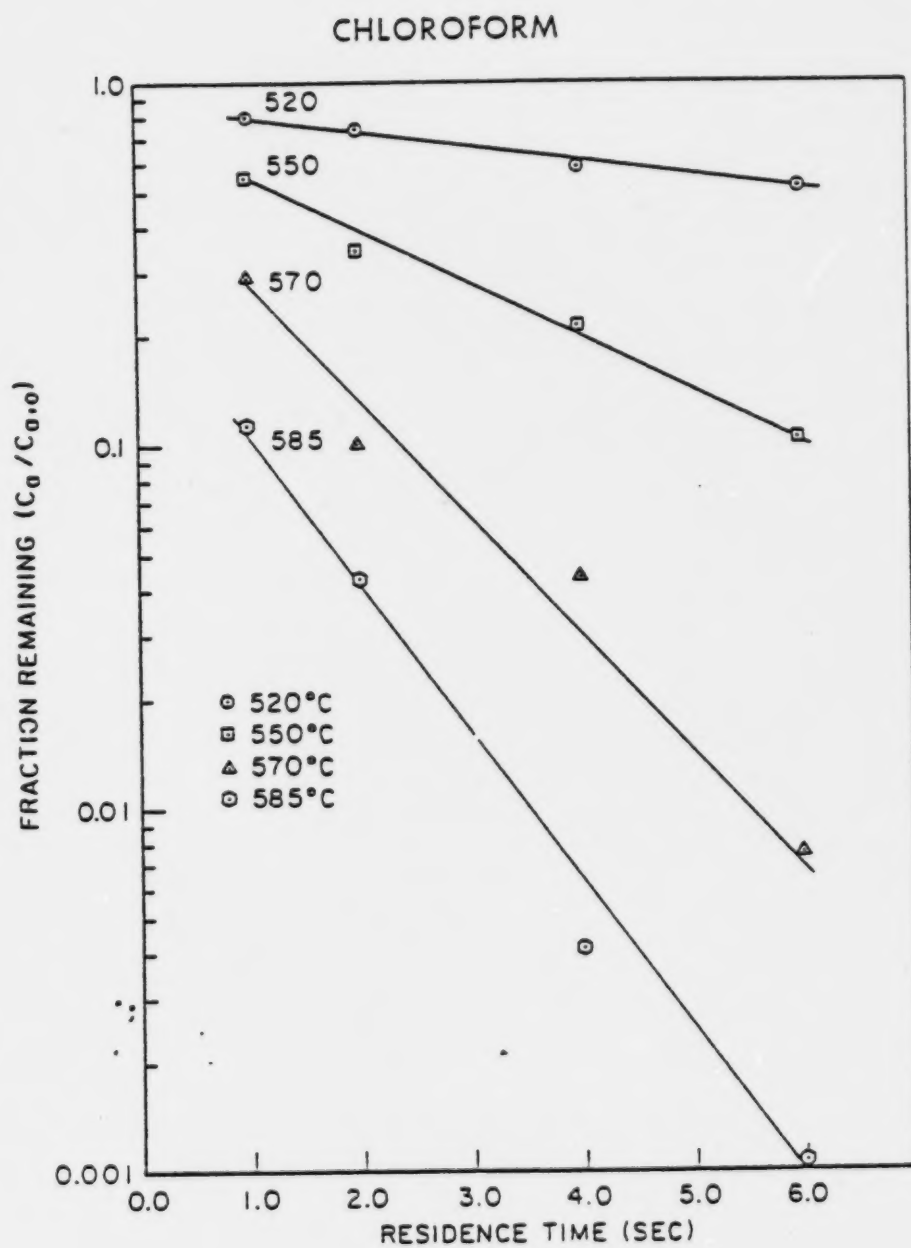


Figure 11. Graph of $\ln f_r$ versus $\bar{t}_r$ at $T = 520, 550, 570, 585^\circ\text{C}$ for Chloroform in Flowing Air.

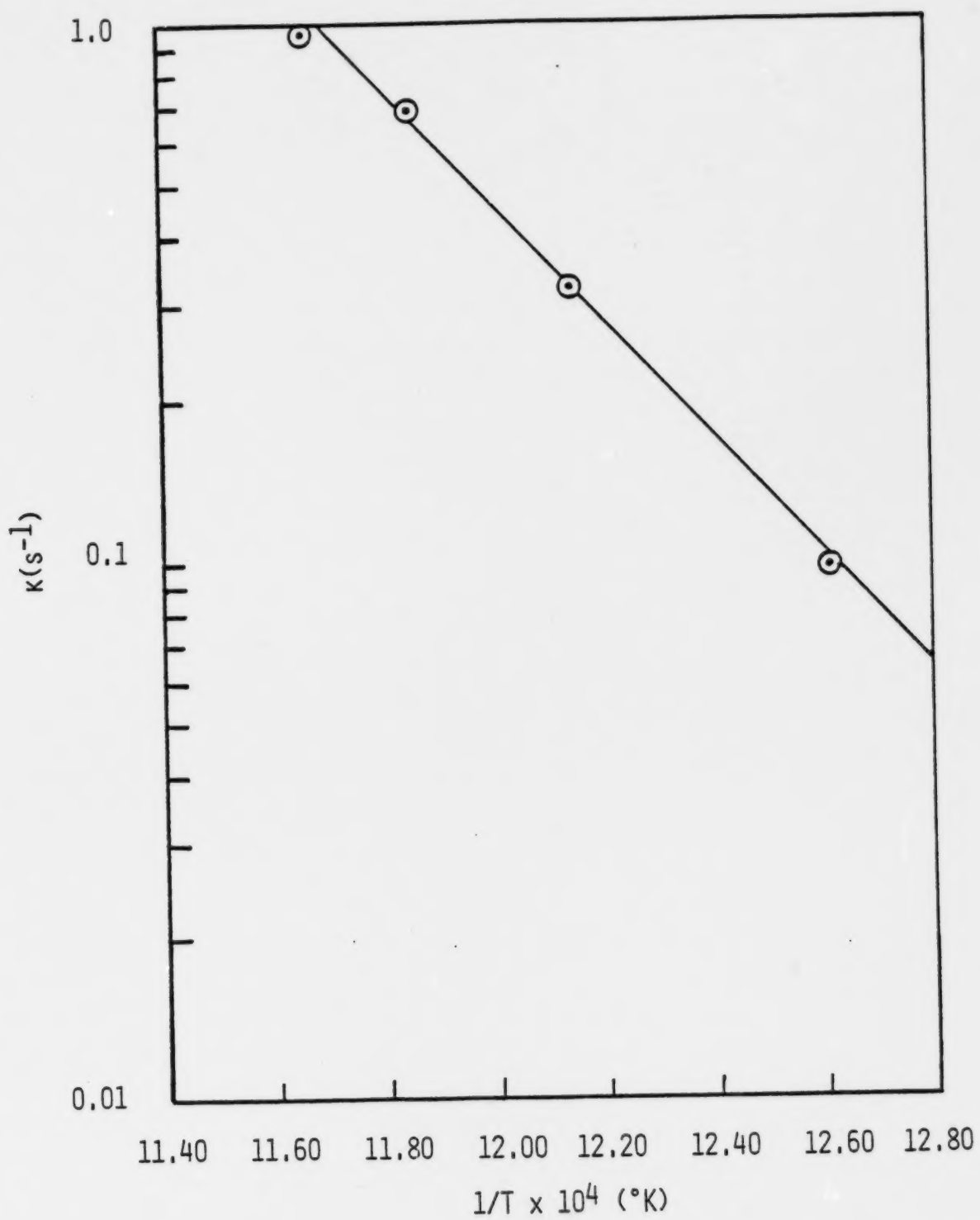


Figure 12. Arrhenius Plot for Chloroform in Flowing Air.

TABLE 3
CHLOROFORM

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time t_r (s)	Exposure Temperature $T(^{\circ}\text{C})$						
	400	500	520	550	570	585	600
1.0	100		81.2	55.7	29.3	11.2	2.29
2.0	100	86.0	74.4	34.8	10.3	4.29	0.24
4.0	100		58.5	21.3	4.27	0.41	0.13
6.0	100		51.0	10.4	0.75	0.108	>0.03

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}\text{C})$	Rate Constant k_1 (s^{-1})	Correlation Coefficient r^2
520	.096	.99
550	.322	.99
570	.693	.98
585	.952	.99
$E_a = 49 \text{ kcal/mole}$		$r^2 = .99$
$A = 2.9 \times 10^{12} \text{ s}^{-1}$		

included in Appendix B. In all cases, the first order kinetic plots yielded far better fits than zeroth or second order plots. The measured kinetic parameters, A and E_a , along with the calculated temperatures for 99% destruction (using Equation 5.8) are listed in Table 4 in order of decreasing $T_{99}(2)$.

FRACTIONAL REACTION ORDER CALCULATIONS

The first order kinetic approach fits the data in the majority of the compounds tested as evidenced by coefficients of correlation, r^2 , from the linear regression analysis are typically greater than .95. However, for certain applications, such as concentration dependence of the destruction rate, a more precise determination of reaction order may be necessary. Thus, a modified treatment of the Van't Hoff method was used to determine the fractional order of the reaction with respect to the parent compound. (18)

Neglecting the pyrolysis term and treating oxygen dependence as previously explained, Equation 5.4 may be expressed in logarithmic form as

$$\log(-d[A]/dt) = \log k' + a \log [A] \quad (5.10)$$

For the decomposition of species A , the order of the reaction, a , can be obtained directly from the graph of $\log(-d[A]/dt)$ versus $\log [A]$. In this investigation, direct concentration measurements were not made. Thus, it was necessary to modify Equation 5.10 such that fraction remaining could be used:

$$\log \left[\frac{-d[A]/[A]_0}{dt} \right] = \log \left[-k' [A]_0^{a-1} \right] + a \log ([A]/[A]_0) \quad (5.11)$$

or

$$\log (\Delta f_r / \Delta t) = \log (-k' [A]_0^{a-1}) + a \log (\bar{f}_r) \quad (5.12)$$

where: $\bar{f}_r$ represents the midpoint fraction remaining over the interval Δf_r .

TABLE 4
SUMMARY OF FIRST ORDER KINETIC RESULTS

Compound	A(s ⁻¹)	E _a (kcal/mole)	Temperature Range	Calculated T ₉₉ (2) (°C)
Acrylonitrile	1.3 x 10 ⁶	31	750-810	910
Acetonitrile	4.7 x 10 ⁷	40	800-850	908
Tetrachloro-ethylene	2.6 x 10 ⁶	33	725-825	900
Methane	3.5 x 10 ⁹	48	700-800	874
Hexachloroben- zene	2.5 x 10 ⁸	41	710-785	845
1,2,3,4- Tetrachlorobenzene	1.9 x 10 ⁶	30	700-765	834
Ethane	1.3 x 10 ⁵	24	675-725	830
Carbon Tetra- chloride	2.8 x 10 ⁵	26	680-730	824
Monochlorobenzene	8.0 x 10 ⁴	23	600-670	810
Dichloromethane	3.0 x 10 ¹³	64	700-755	796
1,2,4-Trichloro- benzene	2.2 x 10 ⁸	39	675-725	789
Pyridine	1.1 x 10 ⁵	24	700-750	767
1,2-Dichloro- benzene	3.0 x 10 ⁸	39	685-725	766
Hexachlorobuta- diene	6.3 x 10 ¹²	59	685-715	763
Benzene	2.8 x 10 ⁸	38	685-720	757
Aniline	9.3 x 10 ¹⁵	71	650-700	726
Nitrobenzene	1.4 x 10 ¹⁵	64	600-650	672
Hexachloroethane	1.9 x 10 ⁷	29	500-600	641
Chloroform	2.9 x 10 ¹²	49	520-585	606
1,1,1-Trichloro- ethane	1.9 x 10 ⁸	32	475-550	601

The fractional order of the reaction can now be determined from the slope of the graph of $\log (\Delta f_r)$ versus $\log (\bar{f}_r)$.

One disadvantage of this differential technique is that the number of data points available for regression analysis is reduced from four to three. It was found that, in general, the variation in the data for the lower experimental temperatures was too great for this type of analysis to produce statistically meaningful results. Furthermore, since it is not known if the reaction order changes with temperature, it was decided to use only the calculated fractional reaction order for the highest temperatures studied. These reaction order calculations are summarized in Table 5 for the twenty (20) test compounds.

TABLE 5
SUMMARY OF FRACTIONAL REACTION ORDER CALCULATIONS

<u>Compound</u>	<u>Temperature (°C)</u>	<u>Reaction Order a</u>	<u>r²</u>
Acetonitrile	850	1.1	1.00
Acrylonitrile	810	1.6	0.98
Aniline	700	1.1	1.00
Benzene	720	1.1	0.90
Carbon Tetrachloride	730	1.5	1.00
Chloroform	585	1.1	0.98
1,2-Dichlorobenzene	725	1.3	1.00
Dichloromethane	752	0.9	0.50
Ethane	725	1.0	0.98
Hexachlorobenzene	785	0.9	1.00
Hexachlorobutadiene	730	1.0	0.99
Hexachloroethane	600	1.2	0.97
Methane	800	1.2	0.93
Monochlorobenzene	670	1.6	0.89
Nitrobenzene	650	1.1	1.00
Pyridine	750	1.3	0.99
1,2,3,4-Tetrachlorobenzene	740	1.3	0.90
Tetrachloroethylene	825	1.1	0.99
1,2,4-Trichlorobenzene	725	1.4	0.99
1,1,1-Trichloroethane	550	1.2	0.96

SECTION 7

DISCUSSION

The data presented in the preceding section represents the only reported systematic direct determination of the thermal stability of a wide range of solid, liquid, and gaseous organic compounds. This data may be used as a guide to determining the ease or difficulty with which these and other wastes may be thermally decomposed.

Other methods of determining the relative 'incinerability' of hazardous organic compounds have been proposed. In the following section we review these proposed methods. We then compare our thermal decomposition data with these rankings. Finally, we present a general interpretation of our kinetic data, its uses and probable limitations, and speculate on the mechanisms of thermal destruction with an emphasis on the use of apparent trends in our data to predict the thermal stability of other hazardous organics.

REVIEW OF PROPOSED INCINERABILITY RANKINGS

Four methods have been proposed to rank the relative incinerability of hazardous organic compounds. Mitre Corporation in conjunction with EPA has proposed a scale based on the heat of combustion per gram molecular weight (H_C /gram of the pure compound) (2). IT Enviroscience has proposed a method based on the laboratory determination of autoignition temperature (AIT) of the pure compound (19). The NBS has proposed a purely theoretical approach based on the kinetics of flame mode thermal decomposition (20). We at the University of Dayton and researchers at Union Carbide have determined in the laboratory the rate of high-temperature, gas-phase thermal

decomposition of pure organic compounds in flowing air (4,5,21,22,23,24). In the paragraphs that follow, the concept behind each of these methods is presented, and we discuss their relevance to incineration along with their advantages and disadvantages.

Heat of Combustion

In the Guidance Manual for Hazardous Waste Incinerator Permits (a preliminary guidance document) the US-EPA presents the heat of combustion per gram molecular weight (H_C/gram) for a hazardous compound as an approximate measure of the incinerability of that compound. When considered in combination with the concentration of the compound in the hazardous waste mixture, the H_C/gram is promoted as a method for selection of the principal organic hazardous constituents in the mixture. Specifically, the hazardous constituent (from 40 CFR Part 261, Appendix VIII) having the lowest heat of combustion value which is present in the waste feed at a concentration sufficient to measure 99.99 percent destruction (the selected compound may be spiked to a sufficient concentration) should be designated a POHC.

The heat (or enthalpy) of combustion of a substance is defined as the heat evolved during combustion of a specified amount of that substance. It is equal to the sum of the heats of formation of the products of combustion at standard state (25°C, 1 atm) minus the heat of formation of the designated compound at standard state. The heat of formation of a compound is simply the standard state enthalpy of the compound when the enthalpy of the elements from which the compound is formed are taken as zero under the same conditions. Whereas the H_C/gram of a compound is always exothermic, the heats of formation may be either exothermic or endothermic. Sign conventions for these values are not standardized so great care is advised when utilizing values from different sources. A list of the H_C/gram values of the hazardous wastes from Appendix VIII is included as Table 6.

TABLE 6

RANKING OF INCINERABILITY OF ORGANIC HAZARDOUS CONSTITUENTS FROM
APPENDIX VIII, PART 261 ON THE BASIS OF HEAT OF COMBUSTION

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Trichloromonofluoromethane	0.11	Bis(chloromethyl) ether	1.97
Tribromomethane	0.13	1,1,1-Trichloroethane	1.99
Dichlorodifluoromethane	0.22	1,1,2-Trichloroethane	1.99
Tetrachloromethane (Carbon tetrachloride)	0.24	Pentachlorobenzene	2.05
Tetranitromethane	0.41	Pentachlorophenol	2.09
Hexachloroethane	0.46	Hexachlorocyclopentadiene	2.10
Dibromomethane	0.50	Hexachlorobutadiene	2.12
Pentachloroethane	0.53	Kepone	2.15
Hexachloropropene	0.70	2,3,4,6-Tetrachlorophenol	2.23
Chloroform	0.75	Dichlorophenylarsine	2.31
Chloral(trichloroacetaldehyde)	0.80	Decachlorobiphenyl	2.31
Cyanogen bromide	0.81	Endosulfan	2.33
Trichloromethanetriol	0.84	Nonachlorobiphenyl	2.50
Hexachlorocyclohexane	1.12	Toxaphene	2.50
Tetrachloroethene (Tetrachloroethylene)	1.19	1,2,4,5-Tetrachlorobenzene	2.61
Cyanogen chloride	1.29	Bromoacetone	2.66
Formic acid	1.32	Dichloroethylene, N.O.S.	2.70
Iodomethane	1.34	1,1-Dichloroethylene	2.70
Tetrachloroethane, N.O.S.	1.39	Chlordane	2.71
1,1,1,2-Tetrachloroethane	1.39	Heptachlor epoxide	2.71
1,1,2,2-Tetrachloroethane	1.39	Phenylmercury acetate	2.71
1,2-Dibromomethane	1.43	Octachlorobiphenyl	2.72
1,2-Dibromo-3-chloropropane	1.48	Acetyl chloride	2.77
Pentachloronitrobenzene	1.62	Trichloropropane, N.O.S.	2.81
Bromomethane	1.70	1,2,3-Trichloropropane	2.81
Dichloromethane	1.70	Dichloropropanol, N.O.S.	2.84
Trichloroethene (Trichloroethylene)	1.74	Dimethyl sulfate	2.86
Hexachlorobenzene	1.79	2,4,5-T	2.87

TABLE 6 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
2,4,5-Trichlorophenol	2.88	Pentachlorobiphenyl	3.66
2,4,6-Trichlorophenol	2.88	1,3-Propene sulfone	3.67
N-Nitroso-N-methylurea	2.89	Methyl methanesulfonate	3.74
Heptachlorobiphenyl	2.98	Aldrin	3.75
1,1-Dichloroethane	3.00	Nitroglycerine	3.79
1,2-Dichloroethane	3.00	2,4-Dichlorophenol	3.81
trans-1,2-Dichloroethane	3.00	2,6-Dichlorophenol	3.81
Phenyl dichloroarsine	3.12	Hexachlorophene	3.82
N-Nitrosoarsine	3.19	Trypan blue	3.84
Azaserine	3.21	Benzotrithloride	3.90
2-Fluoroacetamide	3.24	Cycasin	3.92
Chloroethane	3.25	N-Nitroso-N-ethylurea	3.92
Hexachlorobiphenyl	3.28	Cyclophosphamide	3.97
Bis (2-chloroethyl) ether	3.38	Dichloropropane, N.O.S.	3.99
1,2,3,4,10,10-Hexachloro-1,4,4a,5,7,8a-hexahydro-1,4:5,8-endo, endo-dimethanonaphthalene	3.38	1,2-Dichloropropane	3.99
Benzeneearsonic acid	3.40	Methylparathion	4.00
Maleic anhydride	3.40	Uracil mustard	4.00
1,2,4-Trichlorobenzene	3.40	Amitrole	4.01
TCDD	3.43	Dimethoate	4.02
Dichloropropene, N.O.S.	3.44	Tetraethyl lead	4.04
1,3-Dichloropropene	3.44	4,6-Dinitro-o-cresol and salts	4.06
Endrin	3.46	N-Methyl-N-nitro-N-nitrosoguanidine	4.06
Chloromethyl methyl ether	3.48	Mustard gas	4.06
2,4-Dinitrophenol	3.52	Maleic hydrazide	4.10
Nitrogen mustard N-oxide and hydrochloride salt	3.56	Dinitrobenzene, N.O.S.	4.15
Parathion	3.61	N-Nitroso-N-methylurethane	4.18
2,4-D	3.62	1,4-Dichloro-2-butene	4.27
		Nitrogen mustard and hydrochloride salt	4.28
		Tetrachlorobiphenyl	4.29

TABLE 6 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Hydrazine	4.44	Phthalic anhydride	5.29
Vinyl chloride	4.45	1-(o-chlorophenyl) thiourea	5.30
Formaldehyde	4.47	2-Methyl-2-(methylthio) propionaldehyde-o-(methylcarbonyl) oxime	5.34
Saccharin	4.49	2-sec-Butyl-4,6 dinitrophenol (DNBP)	5.46
3-Chloropropionitrile	4.50	p-Nitroaniline	5.50
DDT	4.51	Chlorobenzilate	5.50
Thiourea	4.51	Dieldrin	5.56
1-Acetyl-2-thiourea	4.55	2,4,5-TP	5.58
Thiosemicarbazide	4.55	Methoxychlor	5.59
Dichlorobenzene, N.O.S.	4.57	4-Nitroquinoline-1-oxide	5.59
Ethyl cyanide	4.57	Diallate	5.62
Bis (2-chloroethoxy) methane	4.60	Daunomycin	5.70
2,4-Dinitrotoluene	4.68	Ethylenebis(dithiocarbamate)	5.70
Isocyanic acid, methyl ester	4.69	3,3'-Dichlorobenzidine	5.72
7-Oxabicyclo (2.2.1) heptane-2,3-dicarboxylic acid	4.70	Pronamide	5.72
Ethyl carbamate	4.73	Aflatoxins	5.73
5-(Aminomethyl)-3-isoxazolol	4.78	Disulfoton	5.73
Methylthiouracil	4.79	4,6-Dinitrophenol	5.74
4,4'-Methylene-bis-(2-chloroaniline)	4.84	Diepoxybutane	5.74
Bis (2-chloroisopropyl) ether	4.93	Dimethyl phthalate	5.74
4-Nitrophenol	4.95	Glycidylaldehyde	5.74
DDE	5.05	Acrylamide	5.75
Dimethylcarbamyl chloride	5.08	3,3-Dimethyl-1-(methylthio)-2-butanone-O-(methylamino)carbonyl oxime	5.82
p-Chloro-m-cresol	5.08	4-Bromophenyl phenyl ether	5.84
Dichloromethylbenzene	5.09	Thiuram	5.85
Trichlorobiphenyl	5.10	Methanethiol	5.91
DDD	5.14	Toluene diisocyanate	5.92
Dimethylnitrosoamine	5.14	Chlorambucil	5.93
N-Nitrosodimethylamine	5.14	Thioacetamide	5.95
Diethylarsine	5.25		

TABLE 6 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
Ethylenethiourea	5.98	2-Butanone peroxide	6.96
Malononitrile	5.98	p-Dimethylaminoazobenzene	6.97
5-Nitro-o-toluidine	5.98	1,4-Naphthoquinone	6.97
Nitrobenzene	6.01	3-(alpha-Acetylbenzyl)-4-hydroxycoumarin and salts (Warfarin)	7.00
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol	6.05	N-Nitrosodietanolamine	7.02
Benzoquinone	6.07	N-Nitrosopiperidine	7.04
N-Nitrosomethylethylamine	6.13	N-Nitrosomonicotine	7.07
p-Chloroaniline	6.14	Phenacetin	7.17
Benzyl chloride	6.18	Ethyl methacrylate	7.27
Resorcinol	6.19	Di-n-butyl phthalate	7.34
Propylthiouracil	6.28	3,3'-Dimethoxybenzidine	7.36
Paraldehyde	6.30	Acetonitrile	7.37
Dichlorobiphenyl	6.36	4-Aminopyridine	7.37
Diethyl phthalate	6.39	2-Chloronaphthalene	7.37
Dioxane	6.41	2 Propyn-1-ol	7.43
2-Methylacetonitrile	6.43	1-Naphthyl-2-thiourea	7.50
N-Nitrosopyrrolidone	6.43	Isosafrole	7.62
Methyl methacrylate	6.52	Dihydrosafrole	7.66
Chlorobenzene	6.60	Safrole	7.68
o-Toluidine hydrochloride	6.63	Auramine	7.69
N,N-Bis (2-chloroethyl)-2-naphthylamine	6.64	Crotonaldehyde	7.73
2,6-Dinitrotoluene di-n-octyl phthalate	6.67	Allyl alcohol	7.75
Reserpine	6.70	Monochlorobiphenyl	7.75
Methyl hydrazine	6.78	Phenol	7.78
Cyanogen	6.79	Phenylenediamine	7.81
Ethylene oxide	6.86	Di-n-propylnitrosamine	7.83
N-Nitrosodietylamine	6.86	Pyridine	7.83
2-Chlorophenol	6.89	Ethyleneimine	7.86
N-Phenylthiourea	6.93	1,1-Dimethylhydrazine	7.87
Acrolein	6.96	1,2-Dimethylhydrazine	7.87

TABLE 6 (continued)

Hazardous Constituent	Heat of Combustion kcal/gram	Hazardous Constituent	Heat of Combustion kcal/gram
N-Nitrosomethylvinylamine	7.91	3,3'-Dimethoxybenzidine	8.81
2-Acetylaminofluorine	7.82	7H-Dibenzo (c,g) carbazole	8.90
Acrylonitrile	7.93	Benz (c) acridine	8.92
Methapyrillene	7.93	Nicotine and salts	8.92
Strychnine and salts	8.03	4-Amino biphenyl	9.00
Methyl ethyl ketone (MEK)	8.07	Diphenylamine	9.09
Cresylic acid	8.09	2-Methylaziridine	9.09
Cresol	8.18	Benzidine	9.18
Toluene diamine	8.24	Benzo (b) fluoranthene	9.25
Acetophenone	8.26	Benzo (j) fluoranthene	9.25
Butyl benzyl phthalate	8.29	Benzo (a) pyrene	9.25
Ethyl cyanide	8.32	Dibenzo (a,e) pyrene	9.33
Bis (2-ethylhexyl) phthalate	8.42	Dibenzo (a,h) pyrene	9.33
Benzenethiol	8.43	Dibenzo (a,i) pyrene	9.33
N-Nitrosodi-N-butylamine	8.46	Fluoranthene	9.35
2,4-Dimethylphenol	8.51	Benz (a) anthracene	9.39
Indenol (1,2,3-c,d) pyrene	8.52	Dibenz (a,h) anthracene (Dibenzo (a,b) anthracene)	9.40
Diethylstilbestrol	8.54	Dibenz (a,h) acridine	9.53
1-Naphthylamine	8.54	Dibenz (a,j) acridine	9.53
2-Naphthylamine	8.54	alpha, alpha-Dimethylphenethylamine	9.54
Methacrylonitrile	8.55	3-Methylcholanthrene	9.57
Isobutyl alcohol	8.62	n-Propylamine	9.58
1,4-Diethylhydrazine	8.68	7,12-Dimethylbenz (a) anthracene	9.61
2-Picoline	8.72	Naphthalene	9.62
Aniline	8.73	Benzene	10.03
1,2-Diphenylhydrazine	8.73	Toluene	10.14

Different values for the H_C will be obtained depending on the phase state of the H_2O in the combustion products. When the H_2O is taken to be in the gaseous or vapor state, the value for H_C /gram is called the lower heating value. This value reflects the retention of energy by the H_2O as it remains in a higher energy state. The values used in the EPA guidance manual are called higher heating values, and relate to H_2O as a liquid product of the combustion process. These values then reflect the heat evolved by H_2O during its condensation from the vapor state to the liquid state and are consistent with the phase of H_2O under standard state conditions.

In determining H_C /gram, one must also consider the phase changes of the selected compound as it undergoes combustion from its standard state condition. This will include energy absorption during both melting and vaporization or sublimation of the compound if it is a solid under standard state conditions. However, the contribution of phase changes to the overall H_C /gram energy balance is normally small in comparison to the energies released during formation of the combustion products.

As previously mentioned, the heat of combustion of a compound is always exothermic. If no heat is being transferred from the combustion system, the release of energy upon combustion increases the temperature of the products themselves. If no heat transfer occurs, the maximum possible temperature of the products, or adiabatic flame temperature, is reached. Since the most efficient flame oxidation occurs at the highest adiabatic flame temperature, it is hypothesized that those compounds which have a high H_C /gram for contribution to the flame temperature are those which will be most easily destroyed. Conversely, those compounds with low H_C /gram

are likely to experience lower flame temperatures and therefore be more difficult to destroy. This rationale is the basis for the US-EPA method of ranking proposed in the guidance manual.

There are several advantages to utilizing H_C/gram as a method of ranking. The experimental determination of H_C/gram utilizes a well established, standardized method which has given rise to a large volume of literature data. Values which are not available in the literature may be calculated based on the formula and structure of the compound of interest and, in addition, the H_C/gram of a mixture may be predicted based on the H_C/gram and concentration of its constituents.

However, there are several shortcomings to the utilization of H_C/gram as a ranking of incinerability. First, H_C/gram as a thermodynamic property does not reflect the chemistry and kinetics of flame-mode combustion. Secondly, the theoretical adiabatic flame temperatures calculated from the heats of combustion of pure compounds are not representative of the temperatures realized in incineration of mixtures of compounds. Thirdly, the method fails to address non-flame destruction modes.

To demonstrate the disparity between the thermodynamic parameter H_C/gram and the chemical and kinetic processes related to combustion, one need only examine the molecule hydrazine as an example. The H_C/gram for this compound on a per gram basis is 4.44 as listed in the guidance manual. Based on this value for ranking incinerability, hydrazine would be considered only slightly less difficult to incinerate than tetrachlorobiphenyl (4.29) and slightly more difficult to incinerate than dichlorobenzene (4.57). The use of hydrazine as a propellant fuel for rocket and jet engines would seem to indicate a failure in this ranking system. In fact, H_C/gram involves the determination of the energy difference between the reactants at equilibrium and the products at equilibrium. However, for large molecules in an incinerator, non equilibrium processes predominate and factors such as the activation energy

must be considered. While the heats of combustion of two compounds may be comparable, the activation energies and rates at which the reaction occurs may be dramatically different.

Secondly, as previously discussed, the H_C /gram of a compound represents complete combustion under carefully controlled physical conditions. Correlation of a parameter obtained under these conditions with the dynamic conditions of the flame zone in an incinerator is risky at best.

In an incinerator, mixtures of waste organics must be vaporized prior to combustion in the flame zone. Adequate oxygen must then be available with sufficient mixing to ensure complete combustion through attack by flame-generated radical species. The presence of products of incomplete combustion in stack effluents indicates that complete combustion of a waste feed is the exception rather than the rule.

As mixtures of compounds rather than pure compounds are being incinerated, the radical pool generated in the flame becomes complex. The degree or completeness of combustion of a waste mixture will be controlled by the rate of reaction with this radical pool which changes with the composition of the mixture. Consequently, the energy available to the flame from the combustion of the mixture will depend on its composition and the route available which presents complete combustion. In this sense, the incinerability of a compound will depend on the other components of the mixture and may change depending on the nature and concentration of those components.

Utilization of H_C /gram as a ranking method also suggests a flame of adiabatic character. However, heat transfer through system components occurs during incineration and even if design considerations could be made to closely approximate an adiabatic flame, at high flame temperatures the dissociation of gaseous products would limit the flame to temperatures significantly less than adiabatic.

Thirdly, although the flame-zone may destroy a waste stream with some efficiency, say 99%, the remaining one percent must be further destroyed at a 99 percent efficiency level to meet a 99.99 percent destruction efficiency. In addition, flame generated radical species combine to form organic species which may be hazardous and possibly more thermally stable than the initial waste stream components. All of these compounds, both input and formed, must then be destroyed in afterburner regions of the incinerator which are primarily non-flame volumes. The first 99 percent of the waste feed is easily destroyed and can probably be handled by practically any existing thermal disposal device. It is the last trace of material which must be dealt with effectively to eliminate hazardous emissions. The process of interest may become non-flame thermal oxidation of gas phase species, whereas H_C/gram is based on flame mode combustion.

Autoignition Temperature

Autoignition phenomenon, or the minimum spontaneous ignition temperature, has been considered for many decades as an indicator of the potential explosion hazard for a given chemical compound (25,26). Well established laboratory procedures are presently available for evaluating the autoignition temperature for combustible organic compounds (26,27). The lowest temperature at which spontaneous ignition occurs under a given set of conditions for a substance is generally designated as the autoignition temperature and of course, this AIT value would vary with different individual organic substances.

Conceptually, the autoignition temperature is the lowest temperature at which a combustible material in the presence of air begins to self-heat at sufficient rate to produce combustion without any other source of ignition. This generally occurs through chain propagation reactions. If heat is produced in a reaction vessel at a rate that is greater than the loss to the containing walls, then the internal heat will rise exponentially and the reaction rate will accelerate as the chain propagation rate is a function of the weakest bond dissociation energy. Therefore, an AIT value may serve

as an indication of bond dissociation energy as related to a combustion chain reaction.

Recently, application of autoignition temperature as a criterion for evaluating the incinerability of different organic substances was suggested (19). Part of the rationale of this suggested ranking method was based upon an earlier observed correlation which involved data obtained from gas-phase thermal decomposition studies and listed autoignition temperatures (22, 23).

There have been several methods proposed for establishing the AIT of a liquid organic chemical and most of these procedures involve the placing of a fixed quantity of liquid in a 0.5 liter flask which has been previously heated in a specially adapted laboratory oven. Through the conduction of a series of tests at converging temperatures, the AIT value can then be established. Experimentally, autoignition is interpreted as the temperature at which a sudden flash of flame or a sharp rise in temperature occurs within the gas environment. The lowest internal flask temperature at which a hot flame ignition occurs for a series of prescribed sample volumes is taken to be the hot flame autoignition temperature. This AIT value varies with the individual test compound, the atmosphere within the flask and the flask internal pressure at the time the sample was admitted.

Briefly, an established procedure for conducting an AIT determination can be summarized as follows: A sample and a clean flask would first be prepared, then a preselected temperature would be established for the initial test. After establishing thermal equilibrium within the flask, a 100 microliter quantity of the test substance would be admitted to the flask interior. At the same time, the lighting within the test region would be subdued so that the analyst could observe the flash that is indicative of the spontaneous ignition. Also thermocouples would be monitoring the temperature within the flask interior. Solid samples can also be tested using this procedure, however, they are generally poured into the flask interior with a special power funnel. Ten minutes are allowed for the ignition to occur. If at this initial temperature

an ignition has not occurred within this ten minute interval, then a different temperature (approximately 30°C higher) would be selected for the next AIT test. This procedure continues in a converging fashion until the AIT value has been obtained, and normally this value will be determined within $\pm 3^\circ\text{C}$.

The details for conducting an AIT determination are clearly established in ASTM method E659-78. The data that are reported for this ASTM method consist of the final apparatus test temperature, the atmospheric pressure, the quantity of sample that was used, the ignition time delay, and the temperature rise.

Over the years numerous chemicals have been subjected to autoignition testing, and these tests have been conducted primarily with the intention of determining the possible explosion hazard that may be presented by an individual chemical compound. The application of the AIT value for ranking industrial organic compounds with respect to ease of incinerability is associated with its self-heating properties, and of course, its ignition due to chain propagation. There are some AIT data for industrial organic waste compounds, and as already stated, there are standard AIT tests that can be conducted for many organic substances. Some recent compilations of data have been presented (19) (see Table 7).

As stated previously, some correlation has been shown between readily combustible organic substances and gas-phase thermal stability. If compounds that have very high AIT values correspond to compounds that have high thermal stability and survivability in an incinerator, and vice versa, then this ranking criteria may be of value. Certainly, compounds that have very low autoignition temperatures would not pose a problem to a high temperature incinerator.

The autoignition temperature for a given compound is dependent upon several key variables. First, the volume of the

TABLE 7
AUTOIGNITION TEMPERATURE
FOR F AND K WASTE CHEMICALS

<u>Chemical</u>	<u>AIT (°C)</u>
Phenol	715
Trichloro-Trifluoroethane (1,1,2-1,2,2-)	680
Methylene Chloride	662
Ortho-dichlorobenzene	648
Chlorobenzene	638
Diphenylamine	634
Methyl chloride	632
Aniline	615
Hexachlorobutadiene	610
Cresylic acid	599
Benzyl chloride	585
Trichlorobenzenes	571
Phthalic anhydride	570
Cresols (m and p)	559
Formic acid	540
Picoline (2-)	538
Hydrocyanic acid	538
Xylene	529
Naphthalene	526
Acrylamide	524
Acetonitrile	524
Benzene	498
Pyridine	482
Nitrobenzene	482
Acrylonitrile	481
Toluene	480
Maleic anhydride	477
Vinyl chloride	472
Acetone	465
Trichloroethane (1,1,1-)	458
Vinylidene chloride	458
Methyl isobutyl ketone	457
Trichloroethane (1,1,2-)	457
Ethyl benzene	432
Isobutanol	427
Ethyl acetate	427
Formaldehyde	424
Cyclohexanone	420
Dichloroethane (1,2-)	413
Ethylene dichloride	413
Epichlorohydrin	411
Trichloroethylene	410
Methyl ethyl ketone	404
Di-n-butylphthalate	403
Methanol	385
N-butyl alcohol	343
Creosote	336
Trichloropropane	304
Trinitrotoluene (2,4,6-)	275
Paraldehyde	238
Cyclotrimethylene tetranitramine	234
Benzotrichloride	211
Cyclotrimethylene trinitramine	197
Nitrocellulose	176
Ethyl ether	160
Carbon disulfide	90

flask is important, as larger volume flasks generally produce higher AIT values. The actual pressure within the flask is a variable, as is the flask oxygen concentration. Normally, these are both atmospheric pressure and air respectively. The composition and thermal conductivity of the flask walls are also important variables.

Autoignition testing would seem to be applicable for comparing substances of relatively low thermal stability, e.g., organic compounds that are readily combusted, and indeed some of the earlier data tend to confirm this. Certainly, testing for autoignition temperature can be accomplished rather quickly as it is a rather straightforward procedure, not requiring highly sophisticated instrumentation.

To use AIT as a criterion for ranking the incinerability of different organic substances would mean that a sequential ranking order would have to be established, and as AIT values are normally hundreds of degrees lower in temperature than the gas-phase environment of an incinerator's afterburner chamber, they would bear little resemblance to the actual test environment. There are several questions that can be raised concerning the application of AIT data for such a ranking system. First, many compounds of interest may not be amenable to examination by the typical AIT test method as the autoignition temperature, if it exists, may be beyond the capabilities of the test apparatus. Here we are speaking of some of the highly halogenated materials such as carbon tetrachloride, brominated biphenyls, and chlorinated naphthalenes, that are fire retardants and actually suppress combustion activity. In addition, there are many waste materials that would be intended for controlled high-temperature incineration disposal that would not be suitable for AIT testing for numerous reasons, e.g., the physical state of the sample, the very high halogen content of the sample, the molecular weight of the compound, and other physical parameters that would inhibit an AIT determination in the laboratory.

Another point to consider is that the atmospheres within an incinerator are often low in oxygen concentration and may have high concentrations of H_2O , Cl_2 , CO_2 , HCl , and organic reactants which may have a pronounced effect upon properties such as the spontaneous ignition of a gas phase sample. Also, most auto-ignition test protocols are not designed for conducting tests with mixtures of organic compounds, and indeed this is what is always happening in the afterburner of a high-temperature incineration system.

For some of the compounds of high interest there apparently are no reported AIT data (see Table 8), and it would seem that AIT testing for some highly halogenated organic substances would not be possible. Also, to conduct an AIT test, it is necessary that the test substance be in the gas phase prior to the spontaneous ignition.

In the ASTM testing for autoignition temperature, there cannot be any foreign substance within the glass flask, nor can there be any condensed phase liquid or solid, as this can adversely affect the AIT measurements. Also, only compounds which produce an exothermic oxidative reaction should be subjected to this type of testing.

For more thermally stable compounds the comparison of gas phase thermal stability to autoignition temperature is questionable. In addition, autoignition testing provides no information concerning the products of incomplete combustion, and in many instances it is these stable products of incomplete combustion that are of interest. Furthermore, AIT testing is not without possible hazards with respect to the toxicity of industrial organic chemicals that will be admitted to the high-temperature flasks.

TABLE 8
F AND K WASTE CHEMICALS FROM
APPENDIX VII WITH NO AVAILABLE AIT

Chemical	Chemical
Acenaphthalene	Ideno (1,2,3-CD) pyrene
Benz (a) anthracene	Meta-dinitrobenzene
Benzo (a) anthracene	Napthoquinone (1,4-)
Benzo (a) pyrene	Nitroglycerin
Benzo (b) fluoranthene	p-chloro-m-cresol
Bis (2-chloroethyl) ether	Pentachlorobenzene
Bis (chloromethyl) ether	Pentachlorophenol
Carbon tetrachloride	Perchloroethylene
Chlordane	Phenolic compounds
Chlorinated fluorocarbons	Phenylenediamine
Chloroacetaldehyde	Phorate
Chloroform	Phosphorodithioic acid esters
Chlorophenol (2-)	Phosphorothioic acid esters
Chrysene	Pyridines
Dibenz (a) anthracene	Tars (polycyclic aromatic hydrocarbons)
Dichlorobenzenes	Tetrachlorobenzene
Dichloroethylene	Tetrachloroethane (1,1,1,2-)
Dichlorophenol (2,4-)	Tetrachloroethane (1,1,2,2-)
Dichlorophenol (2,6-)	Tetrachloroethylene
Dichloropropanols	Tetrachlorophenols
Dimethylphenol (2,4-)	Toluene diisocyanate
Dinitrophenol (2,4-)	Toluene-2,4-diamine
Dinitrotoluene (2,4-)	Toxaphene
Fluoranthene	Trichloroethane
Heptachlor	Trichlorofluoromethane
Hexachlorobenzene	Trichlorophenol (2,4,6-)
Hexachlorocyclopentadiene	Trichlorophenols
Hexachloroethane	Trinitrotoluene isomers

In summary, we are most interested in identifying those substances which have a high survivability in an incinerator (eg., those compounds that might survive the transport through an incinerator system) or those compounds that could be generated during the different fault modes of operation in an incinerator. Autoignition testing that is conducted in an air atmosphere (which has no means of providing any further data other than providing the AIT temperature) does not provide information concerning those compounds that have high survivability, nor is there any information presented concerning possible products of incomplete combustion. In addition, conducting of AIT tests in different atmospheres would be quite difficult. It would be an especially difficult task to conduct AIT testing in an atmosphere that simulated the afterburner section of a high-temperature incinerator.

Theoretical Kinetics

Tsang and Shaub at the National Bureau of Standards have proposed a ranking of incinerability of hazardous wastes based purely upon theoretical consideration of flame mode decomposition kinetics. Their approach focuses upon estimation and extrapolation of elementary reaction rate data that is available from experiment and theory for a limited number of hazardous organics or similar compounds (20). Their kinetic approach is justified on the basis that although thermodynamic calculations indicate complete oxidation of potential POMCs by 500°C, field incinerator results show incomplete oxidation for most POMCs. This implies that kinetics and not thermodynamics is controlling the rate of destruction and measured destruction efficiencies.

Elementary reactions that can destroy POMCs are placed in two broad categories, unimolecular decomposition reactions and bimolecular reactions involving attack of the POMC by small reactive radical species. Unimolecular reactions are further subdivided into bond rupture and complex fragmentation. It is shown through equilibrium calculations of radical concentration for various equivalence ratios that OH is the predominant

reactive radical in fuel-lean situations which are expected to occur within incinerators. It is recognized, however, that H may be present under conditions of poor mixing where a POHC may experience an oxygen deficient environment. Thus, bimolecular processes are subdivided into addition and abstraction reactions involving OH radicals and the POHC.

Several generalizations concerning reaction rates for various classes of compounds are made and are listed below.

- OH addition reactions are electrophilic in nature leading to lowering of rates for unsaturates with increasing halogenation.
- The strength of the bond being broken during abstraction is an important factor with C-H bonds being the usual reaction site.
- H atom addition rates vary little from compound to compound.
- Bond rupture reactions will occur at the lowest energy bond of a given compound and their rates will track the lowest bond dissociation energy of a series of compounds.
- Complex fragmentation is an important destruction mechanism for chloroalkanes through a concerted four-center elimination of hydrogen chloride to form the alkene.
- Substitution of positions greater than α to the bond being broken have little effect on the bond dissociation energies and decomposition rates for unimolecular processes.

Calculation of reaction rates for various compounds indicate thermally stable compounds will be destroyed by radical attack and less stable compounds by unimolecular decomposition. For OH attack to produce a DE of 99.99%, they estimate that typically a temperature of 1,230°K is required. At this temperature unimolecular decomposition by bond rupture is significantly faster than OH attack for compounds with their weakest bonds in the 80-85 kcal/mole range. Since complex fragmentation rates are even faster, they conclude radical attack is only of importance

for simple aromatics and other unsaturated molecules without organic substituents and simple one or two carbon saturated systems. All the bonds in these compounds have dissociation energies greater than 85 kcal/mole. These considerations lead to the ranking of selected compounds in Appendix VIII, Part 261, which has been reproduced in Table 9.

An obvious advantage of the theoretical kinetic approach is that approximate reaction rates can be calculated and the compounds ranked without additional experimentation when adequate data already exists in the literature, although an experienced kineticist is required for the evaluation of the rates. Destruction efficiencies are definitely controlled more by reaction kinetics than thermodynamic equilibrium and from this standpoint the theoretical kinetic approach would appear to be more clearly related to incineration than a thermodynamic approach. The range of chemical kinetics processes have been adequately addressed and appear to be placed in a proper perspective based on step-by-step scientific reasoning. A further advantage is that many of the compounds in Appendix VIII can be ranked by this method. This ranking method was originally developed for application to flame mode destruction but, with modification for lower temperatures in the non-flame zone, may also be of use in developing a non-flame or a combined ranking scale.

The most serious disadvantage to this technique is that it relies primarily on experimental data generated outside the range of conditions experienced in an incinerator. Much of the unimolecular decomposition data is based on shock tube experiments that may have been obtained at significantly higher temperatures than experienced in an incinerator. The bimolecular reaction rate data are generally based on low and room temperature experiments for application to tropospheric chemistry and is about a thousand degrees too low. Extrapolation of this data over such a range may represent a significant source of error.

Another disadvantage is that actual reaction rate specification relies on theoretical calculations of radical concentrations.

TABLE 9

INCINERABILITY RANKINGS OF SOME HAZARDOUS COMPOUNDS FROM
APPENDIX VIII, PART 261 ON THE BASIS OF CHEMICAL KINETICS

<u>Compound</u>	<u>Rationale</u>
hexachlorobenzene pentachlorobenzene chlorobenzene benzene naphthalene vinyl chloride	all C-H bonds in excess of 110 kcals, C-Cl bonds ~95 kcals, OH addition is major destruction mode and is dependent on substituents on unsaturated structure
chloromethane ethylene diamine dichlorophenol resorcinol chlorotoluene formaldehyde acetaldehyde acrolein	C-H bonds are in the 90-93 kcals range. All other bonds are greater than 80 kcals. Assume that OH abstraction is controlling
dimethylphthalate methylethyl ketone allyl alcohol chloroform bromomethane dinitrobenzene trinitrobenzene tribromomethane hexachloropropene hexachloropentadiene bromoacetone hydrazine methylhydrazine	bond breaking processes in the 60-80 kcal range. Unimolecular decomposition is controlling mechanism
1,2-dichloroethane 1,2-dichloropropane hexachlorocyclohexane di-n-butylphthalate ethyl carbonate 1,2-dibromo- 2-chloropropane	low energy pathway through complex fragmentation into stable molecules $A_{\infty} \sim 10^{12}$ - 10^{14} /sec $E_{\infty} \sim 45$ -55 kcal
methyl iodide 1,2-diphenyl hydrazine nitroglycerine O-nitroso-diethylamine 2-butanone peroxide	fragmentation into radicals brought about by very weak bonds 40-55 kcal range. A factor 10^{15} /sec

The limited number of estimated rates which are quoted are calculated for clean systems containing a single organic component. The estimation of radical concentration in a complex system such as an incinerator is much more difficult and consequently less accurate. Such an error could cause a reordering of the stability ranking.

Gas-Phase Thermal Decomposition

The University of Dayton Research Institute and researchers at the Union Carbide Corporation have proposed a laboratory approach to the problem of establishing an 'incinerability' ranking scheme. This approach involves using specialized laboratory thermal analysis equipment to obtain gas-phase thermal decomposition data.

Since 1974, four unique thermal analysis systems have been developed at UDRI to study the gas-phase thermal decomposition of organic materials (6,15,16). In all of the instrumentation systems developed at UDRI, the approach has been to pursue the closed continuous design concept depicted in Figure 13. This approach incorporates considerable flexibility and has found applications in numerous research tasks.

For the purpose of conducting thermal decomposition studies, the thermal unit depicted in Figure 13 is of the form of a quartz tubular flow reactor housed in a three-zone furnace (Thermal Decomposition Unit, TDU). These TDU's are designed such that dilute gas-phase samples are generated and are then subjected to precisely controlled conditions of thermal exposure residence time, pressure, and atmosphere.

At Union Carbide the TDU is a somewhat simpler device and the thermal exposure is less precise than in the UDRI systems. The Union Carbide system also uses a different sample entry mode. Here, special premixed samples are continuously fed to the reactor. This limits the types of samples which may be analyzed by this instrument to high vapor pressure liquids and gases. In the UDRI systems dilute gas-phase samples are generated in special

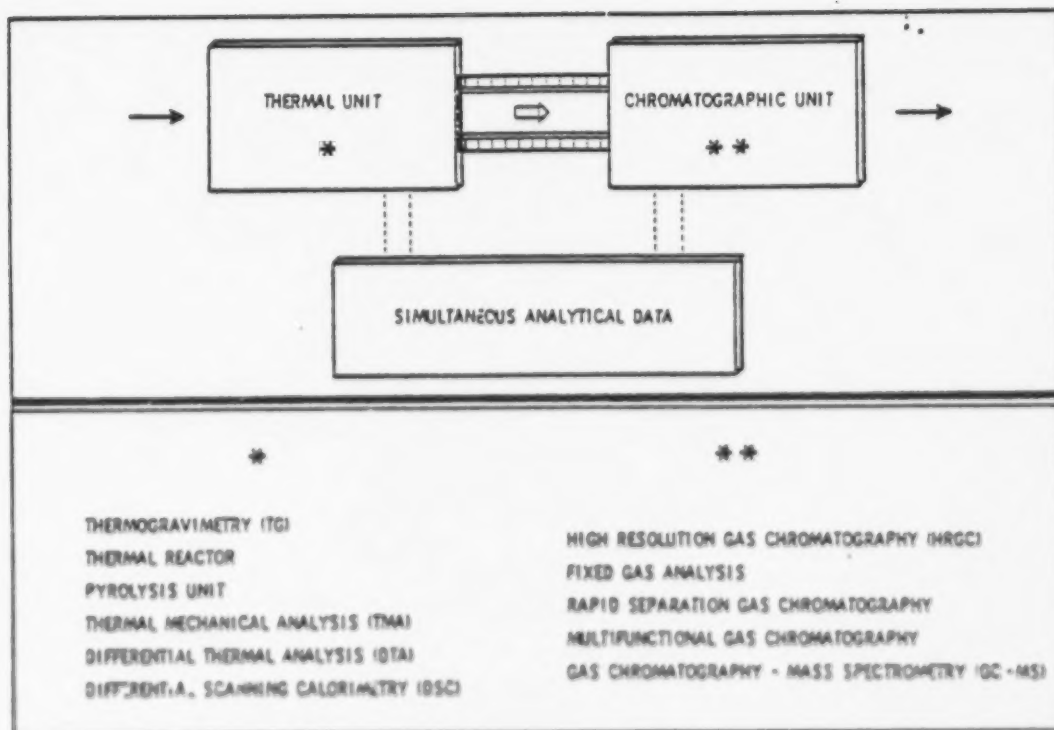


Figure 13. Block Diagram of Basic Closed Continuous System.

heated sample inlet chambers. This permits gas, liquid, and solid samples to be analyzed with equal ease.

The analytical technique employed for analysis of the reactor effluent includes programmed temperature high resolution gas chromatography (HRGC) and gas chromatography-mass spectrometry (GC-MS), in the case of the UDRI systems, as well as total hydrocarbon analysis using a hydrogen flame ionization detector (FID) in the Union Carbide System.

As shown in Figure 13, these thermal analysis systems provide simultaneous data from the TDU and the analytical components. Specifically, the systems determine the quantity of a sample which has survived the thermal exposure and the chemical composition of the effluent. These data are best represented in the form of a thermal decomposition curve.

In order to use the thermal decomposition profiles as a means of ranking the thermal stability of organic compounds a characteristic parameter must be selected which best describes the data. The temperature needed to achieve 99.99% destruction efficiency at a given residence time has been proposed by researchers at Union Carbide (22). Other destruction efficiencies, such as 99%, could also be selected.

The simplest method of determining these temperatures for a specified mean residence time is to extrapolate the thermal decomposition curve to the 99% or 99.99% destruction level. Although this is the most accurate method, the data are only valid for the mean residence time at which the data were taken. For a comparative study, however, this should not be a serious limitation.

In addition to actually measuring various levels of destruction, thermal decomposition data may be taken in such a way as to permit kinetic calculations. Rather than measure the thermal decomposition to very low levels at one mean residence time, the thermal decomposition may be measured to moderate levels at several different mean residence times. From kinetic analysis as

described in Section 5, kinetic parameters may be calculated and the temperature required for a level of destruction at any residence time calculated. Although the temperature for 99.99% destruction efficiency calculated by this method is more sensitive to experimental error than the direct method, this modeled and tabulated information is more versatile.

The kinetic data also allows a somewhat different approach of ranking thermal stability. Instead of the temperature required for a given level of destruction, compounds could be ranked by the measured destruction efficiency at a given temperature. The latter approach would be equivalent to a ranking by pseudo-first order reaction rate constants. The choice of temperature for comparison can be a significant problem. This approach is discussed more thoroughly in the concluding remarks since this section consists of a review of previously proposed ranking methods.

Table 10 ranks the compounds studied at Union Carbide by temperature required for 99.99% destruction efficiency at two seconds mean residence time. All of Union Carbide's work was oriented to taking kinetic data using their simpler instrument. From the published literature it is unclear how the presence of PICs were dealt with in the reduction of these data. Tables 2 and 4 show a ranking of the UDRI studied compounds by the temperatures for 99 and 99.99% destruction efficiency.

The application of a laboratory approach to establishing an incinerability ranking has several distinct advantages. It provides a means by which the thermal stability of an organic material may be measured based on experimental observation. This is of vital importance as the experimental technique allows data to be taken not only on pure substances but on materials in complex mixtures as well. Not only can "real world" samples be examined, but the conditions of atmosphere, mean residence time, and temperature can be readily altered to observe their effect on the thermal decomposition.

TABLE 10

UNION CARBIDE DETERMINED
THERMAL OXIDATION PARAMETERS

Compound	A	E cal/mole	T _{99.99} (2) (°C)
Acrolein	3.30x10 ¹⁰	35900	524
Acrylonitrile	2.13x10 ¹²	52100	703
Allyl Alcohol	1.75x10 ⁶	21400	581
Allyl Chloride	3.89x10 ⁷	29100	649
Benzene	7.43x10 ²¹	95900	717
Butene-1	3.74x10 ¹⁴	58200	646
Chlorobenzene	1.34x10 ¹⁷	76600	744
1-2 Dichloroethane	4.82x10 ¹¹	45600	634
Ethane	5.65x10 ¹⁴	63600	720
Ethanol	5.37x10 ¹¹	48100	680
Ethyl Acrylate	2.19x10 ¹²	46000	589
Ethylene	1.37x10 ¹²	50800	694
Ethyl Formate	4.39x10 ¹¹	44700	619
Ethyl Mercaptan	5.20x10 ⁵	14700	374
Methane	1.68x10 ¹¹	52100	808
Methyl Chloride	7.34x10 ⁸	40900	824
Methyl Ethyl Ketone	1.45x10 ¹⁴	58400	675
Propane	5.25x10 ¹⁹	85200	705
Propylene	4.63x10 ⁸	34200	675
Toluene	2.28x10 ¹³	56500	702
Triethylamine	8.10x10 ¹¹	43200	570
Vinyl Acetate	2.54x10 ⁹	35900	629
Vinyl Chloride	3.57x10 ¹⁴	63300	723

In addition to providing the information for a sequential ranking of thermal stability, thermal decomposition profiles contain important additional information. At a glance the thermal decomposition curve reveals the thermal decomposition behavior of the species of interest under the specified conditions of residence time and atmosphere. When pure compounds are examined, the number and relative quantity of PICs produced by that compound may also be studied. The overall shape of the profile of the parent species reflects the temperature sensitivity of the material. For example, a compound may survive unaffected to a high temperature yet may decompose quite rapidly; vice versa, a material may begin to decompose early yet the thermal decomposition may be quite prolonged and some of the material may survive to a quite high temperature. In short, two compounds may have the same $T_{99.99}$ yet both exhibit very different thermal decomposition behavior. Such information is best presented in the form of the thermal decomposition profile.

As with each of the other proposed incinerability ranking mechanisms, the laboratory approach has some disadvantages. The most often quoted weakness is that the flame mode of destruction is not addressed as laboratory thermal decomposition data have been taken in a non-flame environment. In many cases materials which are excellent fuels and are thus considered easily incinerated based on flame temperature also exhibit a high thermal stability. However, since the majority of wastes are incinerated as mixtures, each of the components will experience the same flame temperature and the kinetics, or gas-phase thermal stability, will control destruction. Indeed, in all of the instances where UDRI data have been applied to actual field studies, good correlation has been observed with respect to the ordering of PCMC stability and the PICs produced (see Appendix B).

Questions have been raised as to the significance of wall reactions in the laboratory determined destruction rates. Although surface reactions may be occurring in an incinerator on particulate matter, these surface reaction rates may be different than those

occurring on the fused silica walls of the laboratory thermal reactions. This question has been raised by researchers at NBS who have noted that the reaction times for unimolecular reactions are comparable to the diffusion times in a 1 mm reactor as used in the laboratory determinations.

However, the key to this problem is the recognition that these experiments are conducted in an oxidizing atmosphere where reaction rates would be expected to typically be a thousand times greater than the majority of unimolecular decomposition rates. Indeed, the observation of a strong oxygen dependence of the decomposition rates indicates these reactions are in the gas-phase. (15)

Furthermore, research has shown that the surface reactivity of silica may be significantly reduced or eliminated by annealing the surface at temperatures in excess of 800°C (28). The surface effects observed in more common metal reactors should not be extrapolated to reactors of quartz construction.

A more practical problem concerns the equipment needed to acquire thermal decomposition data. Thus far this technique has not received interlaboratory standardization in many respects. It is therefore likely that different laboratories using different equipment could get different results. However, while the actual data may vary, the overall ranking should be in good agreement.

COMPARISON OF RANKINGS WITH UDRI THERMAL DECOMPOSITION DATA

The development of a scale of incinerability that a field engineer could easily use in the evaluation of incinerator permits is of the highest priority to EPA. Many parameters can be envisioned which might be appropriate as a basis for such a scale. The proposed rankings reviewed in the previous section represent the most discussed and probably best accepted possibilities for eventually serving as a universal scale of incinerability. For one scale of incinerability to correlate with another scale would be considered additional evidence of its validity. However, correlation with a broad range of incineration data will eventually be required before a proposed ranking will receive universal acceptability.

In this section we compare our laboratory generated gas-phase thermal decomposition data with rankings proposed in the previous section. In the case of the NBS and Union Carbide scales, this process is complicated by lack of overlap of the compounds investigated.

Comparison with Heats of Combustion

Plots of extrapolated $T_{99}(2)$ and $T_{99.99}(2)$ in degrees centigrade versus the heat of combustion per gram molecular weight in units of kilocalories per gram are depicted in Figures 14 and 15, respectively. A numerical summary of the comparative data are included in Tables 11 and 12.

It is evident from these plots that there is extremely little correlation between these data sets. The most obvious observations are the location of the three data points at the lower left of the plots and the data point at the extreme right. The three compounds with low heats of combustion are hexachlorobutadiene, chloroform, and 1,1,1-trichloroethane while the compound with the high heat of combustion is methane. Based on heat of combustion, one would predict the chlorinated compounds to be very stable while methane would be very easily destroyed. It is most striking that the observation is in the exact reverse. The only agreement which can be readily discerned is the general increase in thermal stability with decreasing heat of combustion for the chlorinated benzenes. Other than this group there is not a discernable trend of agreement, either within a class or between classes of compounds.

Comparison with Auto-Ignition Temperature

Plots of extrapolated $T_{99}(2)$ and $T_{99.99}(2)$ in degrees centigrade versus the auto-ignition temperature of the pure compounds in units of degrees centigrade are depicted in Figures 14 and 15, respectively. Numerical comparisons are again given in Tables 11 and 12.

There appears to be a general positive correlation for both $T_{99}(2)$ and $T_{99.99}(2)$ with AIT for those compounds with an AIT

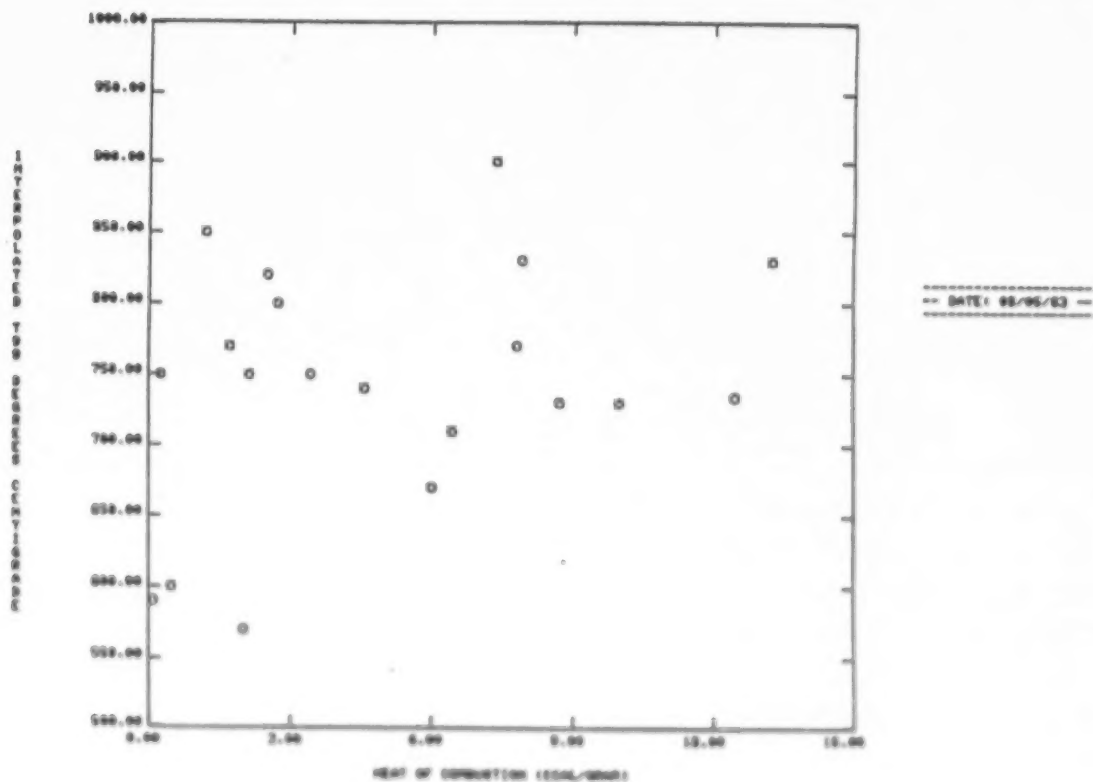


Figure 14. Scatter Plot of Interpolated $T_{99}(2)$ Versus Heat of Combustion for Test Compounds.

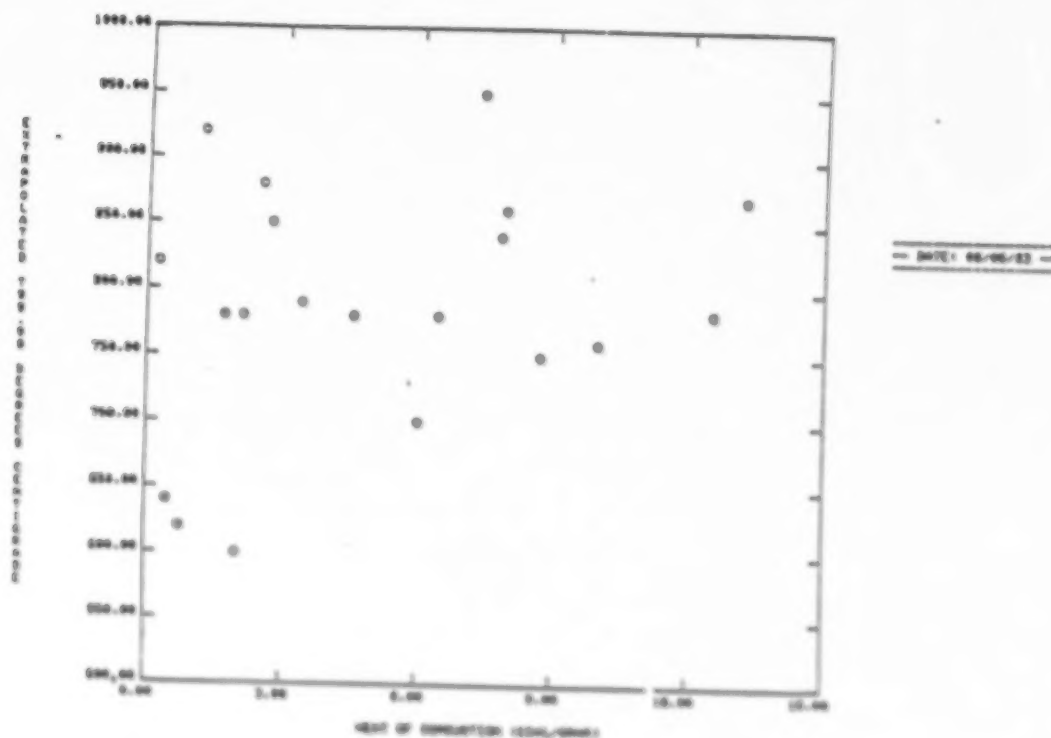


Figure 15. Scatter Plot of Extrapolated $T_{99.99}(2)$
Versus Heat of Combustion for Test Compounds.

TABLE 11

SUMMARY OF THERMAL DECOMPOSITION DATA
CORRELATION PARAMETERS

<u>Parameter</u>	<u>Abbreviation</u>	<u>Units</u>
Interpolated temperature for 99% DE at 2 seconds residence time	T ₉₉ (2)	°C
Extrapolated temperature for 99.99% DE at 2 seconds residence time	T _{99.99} (2)	°C
Heat of combustion per gram mole- cular weight	ΔH_C /gram	kcal/gram
Autoignition temperature	AIT	°C
NBS Theoretical kinetic ranking	NBS	---
Union Carbide calculated T _{99.99} (2)	UC	°C
Heat of Combustion	ΔH_C	kcal/mole
Number of hydrogens	#H	---
Number of chlorines	#Cl	---
Hydrogen to hydrogen plus chlorine number ratio	H/(H+Cl)	---
Chlorine to hydrogen plus chlorine number ratio	Cl/(H+Cl)	---
Hydrogen to carbon number ratio	H/C	---
Chlorine to carbon number ratio	Cl/C	---
Hydrogen to hydrogen plus chlorine mass ratio	M _H /(M _{Cl} +M _H)	---
Chlorine to hydrogen plus chlorine mass ratio	M _H /(M _{Cl} +M _H)	---
Hydrogen to carbon mass ratio	M _H /M _C	---
Chlorine to carbon mass ratio	M _{Cl} /M _C	---
Lowest bond dissociation energy (19,29,30)	LBDE	kcal/mole
Lowest hydrogen bond dissociation energy	LHBDE	kcal/mole
Activation energy	E _a	kcal/mole
Arrhenius coefficient	A	seconds ⁻¹

TABLE 12
SUMMARY OF NUMERICAL VALUES OF THERMAL
DECOMPOSITION CORRELATION PARAMETERS

	$T_{99}(2)$	$T_{99,99}(2)$	$\Delta H_c/MW$	AIT	HBS	U.C.	ΔH_c	H	Cl	H/C	$\frac{H}{(Cl+H)}$	$\frac{Cl}{(Cl+H)}$	$\frac{H}{Cl}$	$\frac{H_{Cl}}{H_{Cl}+H}$	η_H/η_C	η_{Cl}/η_C	E_a	A	LINE	$29, 30$ LITER
Methane	830	870	13.26	573	---	008	213	4	0	1	0	4	0	0	0	.333	48	3.5×10^9	104	104
Dichloroethane	770	780	1.70	662	---	---	144	2	2	.5	.5	2	2	.0274	.973	.167	64	3.1×10^{13}	79	99
Chloroform	590	620	0.75	---	4	---	89.5	1	3	.25	.75	1	3	.00935	.991	.0033	49	2.9×10^{12}	77	96
Carbon Tetrachloride	750	820	0.24	---	---	---	36.9	0	4	0	1	0	4	0	1	0	26	2.9×10^5	70	NA [†]
Benzene	730	760	10.00	498	3	717	781	6	0	1	0	1	0	1	0	.0033	30	2.8×10^8	110	116
Monochlorobenzene	710	760	6.45	639	2	744	726	5	1	.033	.167	.033	.167	.124	.076	.0694	23	1.0×10^4	95	---
1,2-Dichlorobenzene	740	780	4.57	648	---	---	672	4	2	.667	.333	.667	.333	.0534	.947	.0555	39	3.0×10^8	---	---
1,2,4-Trichloro- benzene	750	790	3.42	571 [*] (no.)	---	---	621	3	3	.5	.5	.5	.5	.0275	.972	.0417	39	2.2×10^6	---	---
1,2,3,4-Tetrachloro- benzene	800	850	2.73	---	---	---	589	2	4	.333	.667	.333	.667	.0139	.986	.0270	30	1.9×10^6	---	---
Hexachlorobenzene	820	880	2.51	---	1	---	624	0	6	0	1	0	1	0	1	0	41	2.5×10^8	---	NA
Pyridine	770	840	7.83	482	---	---	619	5	0	1	0	1	0	1	0	.0033	24	1.1×10^5	---	---
Aniline	730	750	8.73	615	---	---	813	8	0	1	0	1.33	0	1	0	.111	71	9.3×10^{15}	80	80
Nitrobenzene	670	700	6.01	482	---	---	740	5	0	1	0	.033	0	1	0	.0694	64	1.4×10^{15}	70	---
Ethane	735	785	12.40	472	---	720	373	6	0	1	0	3	0	1	0	.25	24	1.3×10^5	88	98
1,1,1-Trichloroethane	570	600	1.99	458	---	---	265	3	3	.5	.5	1.5	1.5	.0275	.972	.125	32	1.9×10^8	$\sqrt{73}^{**}$	$\sqrt{73}^{**}$
Hexachloroethane	600	640	0.46	---	---	---	109	0	6	0	1	0	3	0	1	0	29	1.9×10^7	73	NA
Tetrachloroethylene	850	920	1.19	---	---	---	197	0	4	0	1	0	2	0	1	0	33	2.6×10^6	---	NA
Hexachlorobutadiene	750	780	2.12	610	---	---	553	0	6	0	1	0	1.5	0	1	0	59	6.3×10^{12}	---	NA
Acetonitrile	900	$\sqrt{950}$	7.37	524	---	---	303	3	0	1	0	1.5	0	1	0	.124	40	4.7×10^7	91	91
Acrylonitrile	830	860	7.93	481	---	703	421	1	0	1	0	1	0	1	0	.0033	31	1.3×10^6	---	---

[†] Not Applicable
^{*} No Data Specified
^{**} Estimated

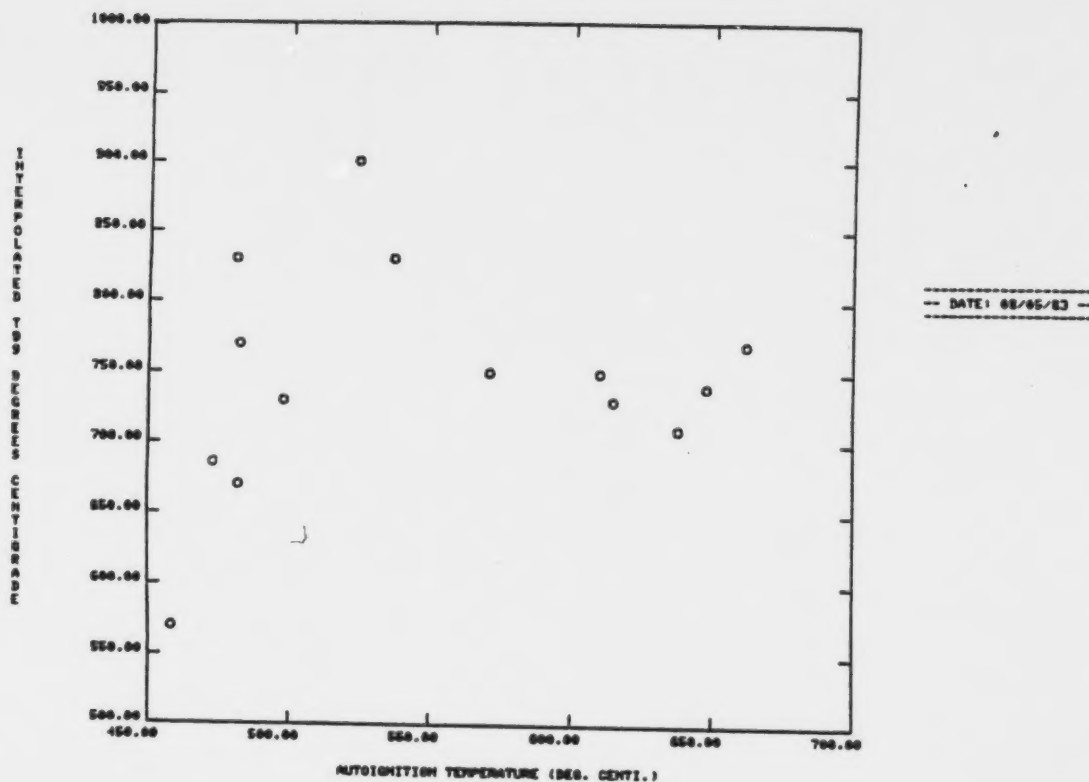


Figure 16. Scatter Plot for Interpolated $T_{99}(2)$ Versus Autoignition Temperature for Test Compounds.

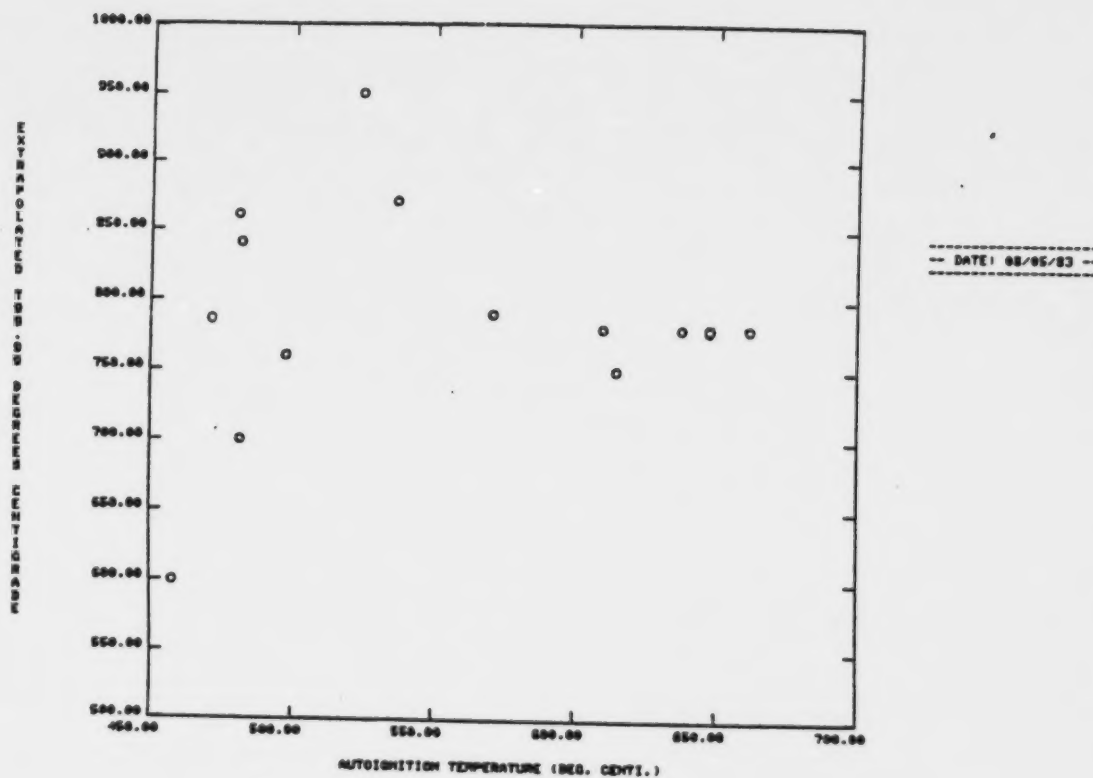


Figure 17. Scatter Plot of Extrapolated T_{99.99(2)} Versus Autoignition Temperature for Test Compounds.

below 550°C. After this temperature, the gas phase thermal stability appears to vary little with AIT. The most positive statement we can make is that there appears to be a positive correlation for the compounds which have a significant fuel value as manifested through their low autoignition temperature.

Researchers at Union Carbide utilized a multiple linear regression for the analysis of their own thermal decomposition data. They concluded that AIT accounted for most of the variability in the thermal stability of the compounds which they studied. The student t-value from the linear regression model for the AIT term was considerably greater than other parameters for which a correlation was performed. To reiterate, our data does not yield a good linear fit of $T_{99}(2)$ or $T_{99.99}(2)$ versus AIT for the full range of compounds investigated.

However, closer examination of the data reveals that, with the exception of monochlorobenzene and methyl chloride, the compounds tested at Union Carbide had autoignition temperatures below 550°C. Thus, both our own and the Union Carbide data yield a positive correlation with AIT when restricted to the same experimental range. The restriction on the Union Carbide data is mainly due to the fact that the compounds with higher AITs could not be easily prepared as premixed gases. From our data for the full range of a representative list of solid, liquid, and gaseous organic compounds, a positive linear correlation does not exist.

Comparison with Theoretical Kinetics Ranking

Direct comparison of our thermal decomposition data is obviously hampered by the fact that only four of the 20 compounds were ranked by the group at NBS. The comparative data is presented in Tables 11, 12, and 13.

The thermal stability of the chlorobenzenes ranked by NBS fall in the same order as suggested by our data based on $T_{99.99}(2)$. One should note that, from our data, the thermal decomposition of monochlorobenzene is initiated at a lower temperature than benzene. This results in a 20°C lower $T_{99}(2)$

TABLE 13
COMPARISON OF NBS RANKING VERSUS
UDRI THERMAL DECOMPOSITION DATA

<u>Compound</u>	<u>NBS Ranking</u>	<u>T_{99.99}(2) (°C)</u>	<u>T₉₉(2) (°C)</u>
Hexachlorobenzene	1	880	820
Monochlorobenzene	3	780	710
Benzene	4	760	730
Chloroform	14	620	590

for monochlorobenzene although its $T_{99.99}(2)$ is 20°C higher. The ranking of the chlorinated benzenes by NBS is based on susceptibility to electrophilic attack by OH radical, with the trend being decreasing susceptibility with increasing chlorination. Their ranking might be extrapolated to other chlorinated benzenes which does indeed agree with our data. However, their ranking did not include other isomers probably due to uncertainty concerning resonance stabilization of the di, tri, and tetra-chlorinated species.

Chloroform was predicted to be rather unstable due to the relatively low energy carbon-chlorine bond. This thermal instability is evident from our results, although it appears to probably be even more fragile than predicted by the NBS ranking.

Comparison Versus Union Carbide Ranking

Only five compounds were examined by both UDRI and Union Carbide. Comparative data is summarized in Tables 12 and 14.

The most apparent discrepancy is for acrylonitrile which is the least stable of the five compounds based on the Union Carbide calculated $T_{99.99}(2)$, while our data indicates its thermal stability rivals that of methane. Ethane is slightly less stable than monochlorobenzene, as measured by Union Carbide, while this trend is reversed in our data, although the difference is small. With the exception of acrylonitrile, the two rankings are similar although our data predicts the compounds to be typically more stable by 40°C.

A plausible explanation for this difference is in the fact that the two data sets were obtained over a different range of mean residence times. Our data were obtained between 1.0 and 6.0 seconds, while the Union Carbide data were for reported residence times between 0.25 and 4.0 seconds. As one can ascertain from the plots shown in Appendix B, there appears to be a reduction in the decomposition rate between 3 and 6 seconds. Since our data covers this range of times while Union Carbide does not, one would calculate a slower first order rate constant from our data. This would

TABLE 14
SUMMARY OF UNION CARBIDE AND UDRI
COMPARATIVE THERMAL DECOMPOSITION RESULTS

Compound	Union Carbide Data				UDRI Data			
	Rank	Calc. $T_{99.99}(2)$ (°C)	E_a (kcal/mole)	A (sec ⁻¹)	Rank ¹	Extr. $T_{99.99}(2)$ (°C)	E_a (kcal/mole)	A (sec ⁻¹)
Methane	2	808	52.1	1.7×10^{11}	4	870	48	3.5×10^9
Monochlorobenzene	3	744	76.6	1.3×10^{17}	11	780	23	8.0×10^4
Ethane	5	720	63.6	5.7×10^{14}	10	785	24	1.3×10^5
Benzene	6	717	95.9	7.4×10^{21}	15	760	38	2.8×10^8
Acrylonitrile	8	703	52.1	2.1×10^{12}	5	860	31	1.3×10^6

result in higher predicted temperatures for 99.99% DE, which is the observed trend. This shift in the range of measurement would almost certainly be responsible for the considerably different kinetic parameters, E_a and A , calculated from the two data sets.

Acrylonitrile deserves special discussion as it possesses easily the most unusual thermal decomposition behavior of all the 20 compounds we tested. First of all, acrylonitrile was observed to form a single product of incomplete combustion in very high yields. Such a PIC could be expected to affect thermal decomposition behavior differently for various mean residence times as in our study versus the Union Carbide study. Secondly, we determined the fractional reaction order for acrylonitrile to be approximately 1.6. This would make the decomposition reaction very concentration dependent. Thus, differences in experimental conditions would also be expected to dramatically affect results. Other researchers have found acrylonitrile to behave in an unusual manner, and we feel that its behavior is too poorly understood to be used for an intercomparison of ranking methods [14].

INTERPRETATION OF GAS-PHASE THERMAL DECOMPOSITION RESULTS

It is apparent from the discussion in the previous section that none of the already proposed scales of incinerability adequately describes our gas-phase thermal decomposition data. Although it was suspected at the outset that our data could not be correlated with a single parameter, we still attempted a series of correlations because of the obvious benefits of success. The dependent and independent variables used in these correlations are identified in Table 11 and the values used are summarized in Table 12. For all of the independent variables identified, correlations were performed versus the extrapolated $T_{99}(2)$ and $T_{99.99}(2)$ as dependent variables.

When all of the test compounds were considered, statistically significant correlations were not obtained for any of the listed parameters. Although actual plots were made, in the interest of brevity they have not been included.

Interestingly enough, the strongest correlation was for interpolated $T_{99}(2)$ and extrapolated $T_{99.99}(2)$ versus the heat of combustion in kcal/mole. These plots are shown in Figures 18 and 19, respectively. In general, the strongest deviation from the observation of increasing thermal stability with decreasing heat of combustion is for those compounds which are poor fuels on a molar basis. This is opposed to the heat of combustion per gram molecular weight scale proposed by EPA for which there was no observable correlation.

In spite of the fact that no single parameter could be identified which correlated with all of our thermal decomposition data, trends were observable in homologous subgroups. By careful consideration and utilization of the principles of chemical reactions, it is possible to explain the behavior of each of the twenty compounds on a relative basis and identify possible mechanisms that can be used to extrapolate this limited data to other compounds not studied in the laboratory. Before introducing such a discussion, it is first useful to discuss the limitations as well as the uses of the data presented in this report such that it can be properly interpreted and placed in perspective.

It should be remembered that all of the thermal decomposition data were obtained for pure compounds in dried flowing air ($\sim 21\% \text{ O}_2$), with a square wave temperature profile, and a very narrow residence time distribution. As such, the reported thermal decomposition profiles and high temperature kinetics are not meant to be representative of a simulated full-scale incinerator. On the contrary, these data have been obtained under well characterized, precisely controlled conditions which can never be realized in a full or pilot-scale unit. Thus, the data reported here are more flexible in that it can be more easily modeled to different

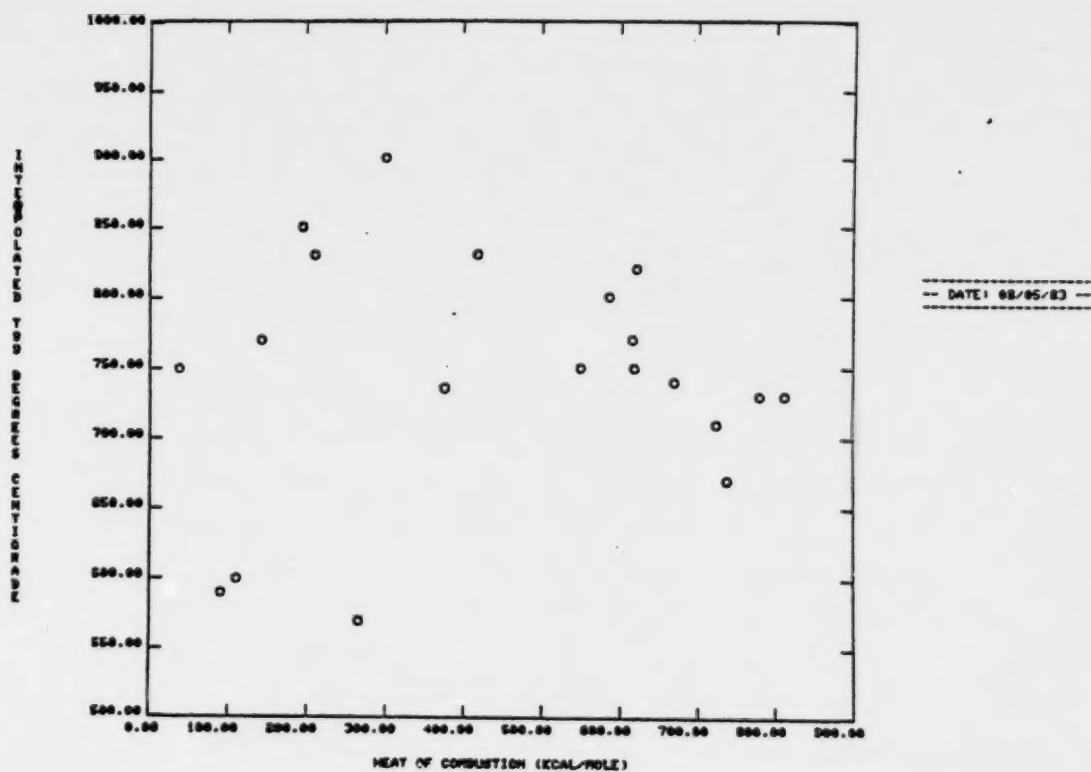


Figure 18. Scatter Plot of Interpolated T₉₉(2) Versus Molar Heat of Combustion.

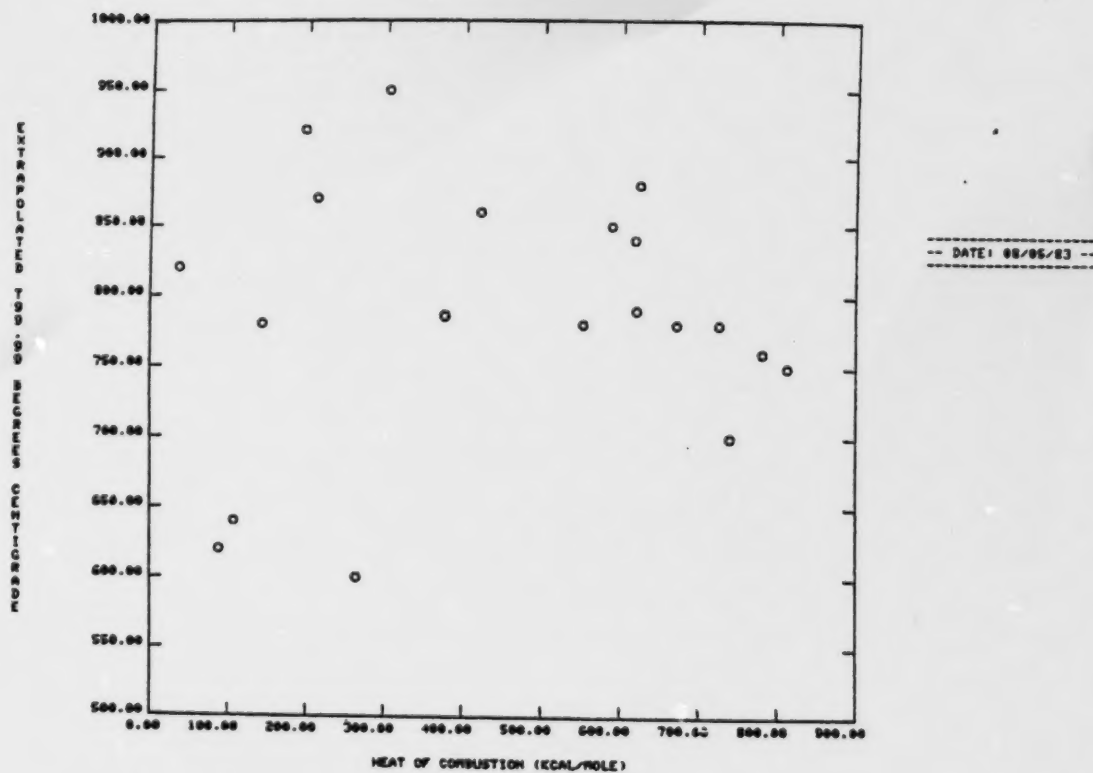


Figure 19. Scatter Plot of Extrapolated $T_{99.99(2)}$ Versus Molar Heat of Combustion.

incinerator designs, and consequently changing incineration conditions, than data from poorly characterized larger-scale units.

The time and temperature data for each of the twenty compounds has been fit to a pseudo first order decomposition kinetic model. This model has been found to adequately describe the behavior of these compounds although it is certainly not a perfect model. In general, a positive curvature was observed in the plots of $\ln f_r$ vs $\bar{t}_r$, which is indicative of reaction orders greater than one. The best fit straight line for these plots intercept the y axis at values of fraction remaining less than one. One would expect an extrapolated intercept at a value of one or greater. This is a further indication of the deviation from exact first order kinetics.

To compensate for this deviation, we have included calculations of the high temperature fractional reaction orders displayed in Table 15. With a few exceptions, the reaction orders vary between 1 and 1.2. It is possible to obtain kinetic parameters based on these fractional order kinetics as opposed to the first order kinetic parameters which we have reported. However, the scope of this study was such that only four residence times were run to determine rate constants at each temperature, and only four temperatures were investigated to determine the Arrhenius coefficients and activation energies. Having only four data points per rate determination, a more precise analysis can not be statistically justified. Also, the precision of the determination of the pseudo first order kinetic parameters is such that the numerical values of these parameters should be used only in an overall descriptive or predictive model of the results and not as an indication of the mechanisms of the fundamental decomposition reactions.

The most significant manifestation of non-first order kinetic behavior would be a concentration dependence of measured destruction efficiencies. The behavior of $\ln f_r$ as a function of initial POHC concentration, $[A]_0$, for different reaction orders, n , is given by the expression

$$\ln f_r = \left(\frac{1}{1-a} \right) \left[\ln(k(a-1)\bar{t}_r [A]_0^{a-1} + 1) \right] \quad a \neq 1 \quad (7.2)$$

where k is the a th order rate constant and other parameters are as previously defined.

The variation of $\ln f_r$ or destruction efficiency with initial POHC concentration will, in general, be small for the compounds tested. A representative summary is presented in Table 15. As one can see from the table, in general the shifts will be small for even a ten fold increase in concentration. However, for apparently isolated cases, such as acrylonitrile, the concentration dependence can be significant and cannot be ignored completely. The table of fractional reaction orders may be used as a guide to the concentration sensitivity of the destruction efficiency of the compounds.

The effect of variation or distribution of incineration conditions is of far greater practical significance. The equations presented in Section 6 explicitly consider three parameters; time, temperature, and oxygen concentration. It is essential that the kinetic data developed and presented in this report be applied to incineration properly. Proper application must include using, at least in some simplified form, the distribution of these parameters.

We are in practice interested in calculating an average destruction efficiency, $\overline{DE}$, for some given set of distribution parameters, $g(\tau_1)$, $g(\tau_2)$, . . . $g(\tau_n)$. The most general form for calculating such a value is

$$\overline{DE} = \int_{\tau_1} \int_{\tau_2} \cdots \int_{\tau_n} DE(\tau_1, \tau_2, \dots, \tau_n) g(\tau_1) g(\tau_2) \cdots g(\tau_n) d\tau_1 d\tau_2 \cdots d\tau_n \quad (7.3)$$

where $DE(\tau_1, \tau_2, \dots, \tau_n)$ may be an analytical expression for destruction efficiency as a function of τ_1 through τ_n , and

TABLE 15
EFFECT OF POHC CONCENTRATION ON $T_{99.99}(2)$

<u>Compound</u>	<u>Reaction Order</u>	<u>$\Delta T_{99.99}^{\dagger}(2)$ ($^{\circ}\text{C}$)</u>
Benzene	1.1	-10
Monochlorobenzene	1.6	-30
1,2-Dichlorobenzene	1.3	-20
Hexachlorobenzene	~ 1.0	~ 0
Aniline	1.1	-10
Hexachlorobutadiene	1.0	~ 0
Chloroform	1.1	-10
Acrylonitrile	1.6	-65

$\dagger$ Calculated for a tenfold increase in initial POHC concentration

$g(\tau_1) \dots g(\tau_n)$ are distribution functions for the variables τ_1 through τ_n .

Let us express this general equation for the specific case of a discrete oxygen distribution. Using destruction efficiency relations derivable from the equations in Section 6, we can derive the expression below:

$$\overline{DE} = 100 - 100 \sum_i \rho_i \exp \left[-t_{r,i} A \left(\frac{CO_{2,i}}{.21} \right)^b \exp (-E_a/RT) \right] \quad (7.4)$$

where: ρ_i is the probability of O_2 concentration.
 $CO_{2,i}$ and residence time, $t_{r,i}$, with the other variables being as previously defined.

For hexachloroethane we can calculate using Equation 6.9, that the temperature required for 99.99% DE is 682°C when subjected to conditions of a square wave temperature profile, almost delta function residence time distribution with $\bar{t}_r = 2.0$ seconds, and an atmosphere of flowing air. A typical incinerator may have a mean oxygen concentration of 8% and a mean gas phase residence time of 2.0 seconds, but the distribution of the variables may be large. Gas phase residence times may be reduced by poor atomization by nozzles, POHCs being sealed in particulate matter, and other means. Oxygen levels experienced by POHCs on the molecular level may even be substoichiometric through poor mixing or formation of bursts of organic material through vaporization or partial oxidation. All of these factors can be handled with laboratory generated kinetic data and scaling equations of the form of 7.3 and 7.4.

We might assume that 90% of the hexachloroethane molecules experience bulk conditions of $t_r = 2.0$ seconds and oxygen levels of 8%. The remaining 10% of the molecules experience a residence time of 0.2 seconds and oxygen levels of 1%. This leads from Equation 7.4 to a calculated destruction efficiency at 682°C (for which

DE = 99.99% when $\bar{t}_r = 2.0$ s and $\text{CO}_2 = 21\%$) of only 87.8% which is between two and three orders of magnitude drop in destruction efficiency. Even if only 1% of the molecules experience these conditions, the DE is only 96% which is still over two orders of magnitude lower. The power of this type of calculation can be further demonstrated when we calculate that the temperature required for 99.99% DE is $1,200^\circ\text{C}$ when $\bar{t}_r = 0.2$ seconds and $\text{CO}_2 = 1\%$. Thus, a rather fragile molecule such as hexachloroethane ($T_{99.99(2)} = 640^\circ\text{C}$) may actually require temperatures in the neighborhood of $1,200^\circ\text{C}$ to assure 99.99% DE under practical incineration conditions. Laboratory data may be extrapolated to field conditions using simple models when these field conditions have been measured or can be estimated with some degree of accuracy.

With these considerations in mind, we can now consider examination of the possible mechanisms involved in the thermal decomposition of the 20 test compounds. Such an examination is useful if we can develop a sufficient understanding of the mechanism that we can extrapolate from the 20 test compounds and predict how other compounds will fall into our incinerability ranking.

For a system containing nitrogen, oxygen, and a mixture of organic compounds, we can classify all chemical reactions resulting in the destruction of parent compound A as unimolecular or bimolecular. Unimolecular decompositions, which involve only the parent species A at the transition state of the reaction, do not involve molecular oxygen or radical attack on species A.

Bimolecular reactions which can result in the destruction of species A, may in principal, involve reactions with molecular oxygen or attack by any number of unstable radicals or intermediates formed in the course of the overall decomposition reaction. Of the potential reactive radical species which may be produced that can affect the destruction of the parent species A, only H, O, and OH would be expected to be formed in significant concentrations. We can furthermore assert that based on

equilibrium calculations alone, OH will be the dominant reactive radical under incineration conditions. Only in extremely fuel rich or lean conditions will this change. Furthermore, abstraction reactions involving H tend to be quite similar to reactions involving OH attack and we would at least qualitatively be describing H processes by considering only OH processes (20).

The kinetic expression for these three destruction processes are summarized in Figure 20 along with examples of each fundamental reaction mechanism. We would expect the relative rate of each of these processes to vary with the molecular structure of the reaction substrate A. Since existing unimolecular decomposition data (shock tubes) is typically obtained at temperatures much higher than those encountered in incinerators and OH attack rates (atmospheric reaction) at much lower temperatures, purely theoretical considerations, although useful, are subject to several sources of error. However, by analyzing the data on these 20 compounds in light of these reaction mechanisms and application of the principles of organic chemistry, we can explain our observations and use this information to provide more educated predictions of thermal decomposition behavior of untested compounds.

Based on this idea, we may group the test compounds in homologous series and explain their relative thermal stability within these subclasses. We have divided the 20 test compounds into five subclasses; these classes are discussed in the following paragraphs.

Methane, Dichloromethane, Chloroform, and Carbon Tetrachloride

The observed trend in this group is decreasing thermal stability with increasing chlorine substitution, except for carbon tetrachloride which is intermediate in thermal stability between methane and dichloromethane. Heat of combustion and AIT agree with this trend. Union Carbide has only obtained data on methane. The NBS ranking of this group is based on the

$$\frac{-d[A]}{dt} = k_1[A] + k_2[A][O_2] + k_i[A][\cdot OH]$$

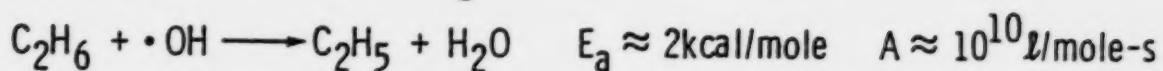
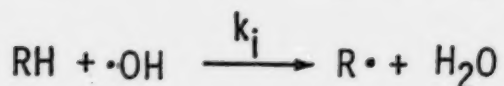
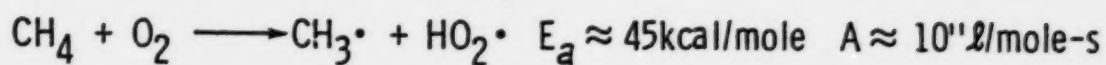
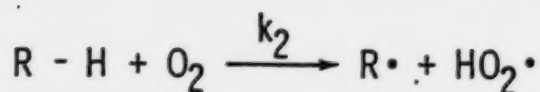
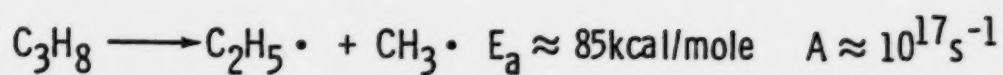
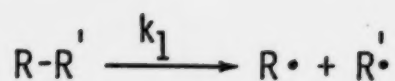


Figure 20. POHC Thermal Decomposition Mechanisms.

lowest bond dissociation energy. The carbon hydrogen bond in methane has a bond dissociation energy (BDE) of 104 kcal/mole. The carbon chlorine bonds in the other three compounds are 79, 77, and 70 kcal/mole, respectively, with the carbon chlorine bonds weakening with increased chlorine substitution. Once again, this is not in agreement with the experimental observations.

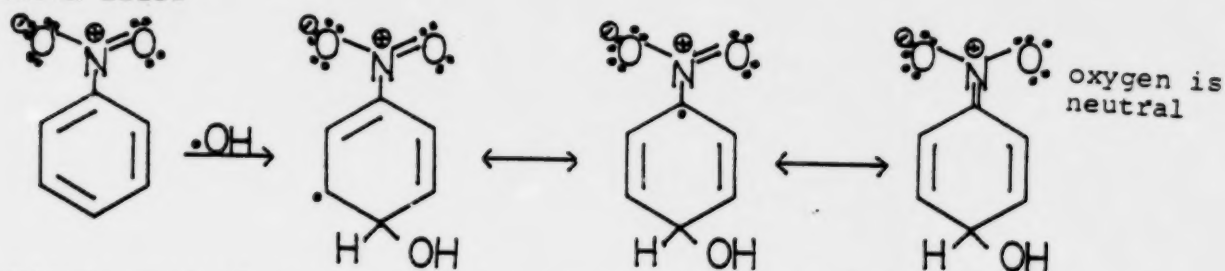
Our data is in agreement with a mechanism based on abstraction of a hydrogen, probably by OH. Since the carbon-hydrogen BDE decreases with increasing chlorine substitution up to chloroform, we would predict decreasing thermal stability which is in fact observed. However, carbon tetrachloride contains no hydrogens and thus would not be susceptible to this mode of attack. It would instead be expected to decompose by bond rupture. The implication of this data set is that H abstraction reaction rates may be faster at these temperatures than previously expected.

Benzene, Monochlorobenzene, 1,2-Dichlorobenzene, 1,2,4-Trichlorobenzene, 1,2,3,4-Tetrachlorobenzene, Hexachlorobenzene, Pyridine, Aniline, Nitrobenzene

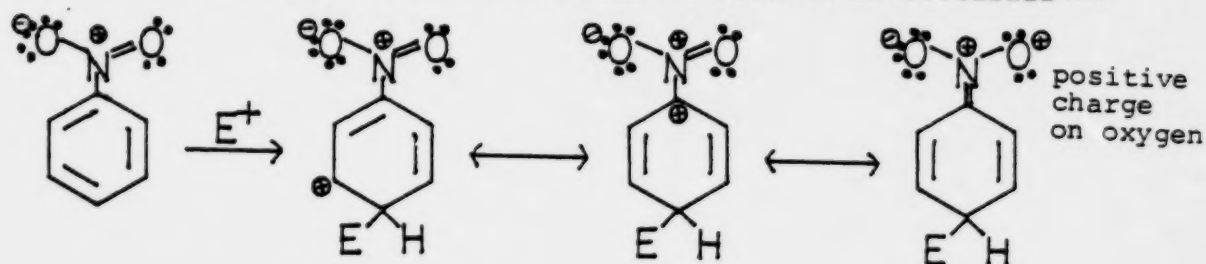
The observed trend is increasing thermal stability with increasing chlorine substitution. Pyridine is more stable, nitrobenzene is less stable, and aniline is about the same thermal stability as benzene. All of the bonds in benzene, the chlorinated benzenes, and pyridine are probably in excess of 90 kcal/mole and we would expect electrophilic addition to be the predominant reaction path. The chlorines and the nitrogen in pyridine are more electronegative than hydrogen or carbon which leads to a destabilization of the electron deficient intermediate resulting from OH addition, thus reducing the rate of decomposition and resulting in a greater thermal stability than benzene.

In the cases of aniline and nitrobenzene, their stability relative to benzene can also be explained by electrophilic attack by a radical such as OH. However, the effect of resonance interaction is somewhat different than in normal

electrophilic attack by a cation. The radical intermediate formed by nitrobenzene is actually stabilized by resonance as shown below

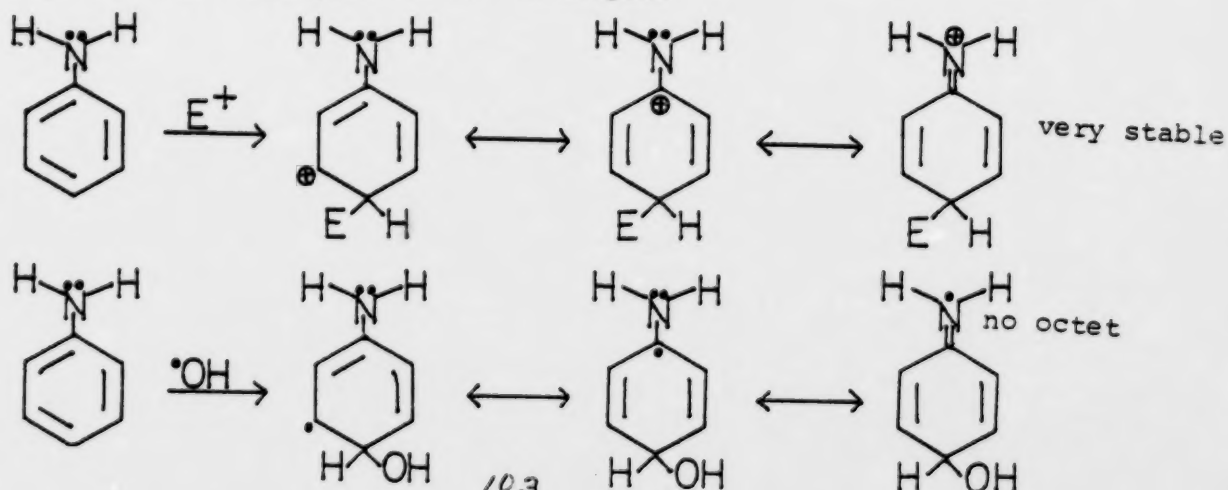


This is opposed to the normal situation for cationic electrophilic addition where nitro substitution results in destabilization



because a positive charge is placed on the electronegative oxygen. This stabilization of the intermediate again leads to a less stable molecule versus benzene. Also in nitrobenzene, the nitrogen carbon BDE is 70 kcal/mole which may be easily broken and does represent an alternative mode of decomposition.

The radical intermediate formed by OH attack on aniline would not receive significant resonance stabilization due to lack of an octet on the normally very stable resonance structure involving the lone pair on the nitrogen.



On this basis we would expect aniline to be about as stable as benzene which is observed. The nitrogen hydrogen BDE is only 80 kcal/mole and may have some role in the decomposition; however, the similarity in stability versus benzene indicates that electrophilic addition is the predominant mode of destruction.

Ethane, 1,1,1-Trichloroethane, Hexachloroethane

One might expect ethane to be destroyed by unimolecular decomposition through bond rupture at the weakest bond. The carbon carbon BDE in ethane is 88 kcal/mole compared to the carbon hydrogen BDE in methane of 104 kcal/mole. Thus, we would predict significantly less stability than methane but still moderate thermal stability for ethane.

Although similar in structure, we expect the pathway for decomposition for 1,1,1-trichloroethane to be by concerted elimination of HCl which is a very low energy process. Based on this we would expect this compound to be one of the least stable we have studied which is in fact the case. Hexachloroethane would have to eliminate Cl₂ to proceed by a concerted pathway. This process is more endothermic and the decomposition of hexachloroethane would instead be expected to proceed through carbon chlorine or carbon carbon bond rupture, both BDE being approximately 73 kcal/mole. Based on these considerations one would expect hexachloroethane to be intermediate in stability between ethane and 1,1,1-trichloroethane, which is the observed trend.

Tetrachloroethylene and Hexachlorobutadiene

Both of these compounds are quite stable. This is probably due to the large BDEs caused by sp² hybridization of all carbon atoms and the lack of hydrogen atoms available for abstraction by OH or formation of OH. Carbon Carbon BDEs would be expected to decrease in the order tetrachloroethylene > hexachlorobutadiene > ethane. This may be used to explain the relative stability of the series.

Electrophilic addition of OH, however, may be the predominant mode of attack in an incinerator. The prediction is

the same since butadiene can form an allyl radical intermediate which is known to be quite stable. This leads to the current prediction that hexachlorobutadiene would be less stable than tetrachloroethylene which agrees with experimental observation.

Acetonitrile and Acrylonitrile

These compounds are very stable and all BDEs are 93 kcal/mole or greater. Based on a mechanism of bond rupture, one might predict acetonitrile to be less stable than acrylonitrile for the C-H bonds would certainly be stronger in acrylonitrile. This reasoning would also apply to H abstraction reactions.

Carbon nitrogen triple bonds are expected to be much less reactive towards electrophilic addition than double bonds. Apparently, the only mode of decomposition for acetonitrile is loss of a hydrogen through bond rupture or abstraction. These are both high energy processes which account for its stability. Acrylonitrile may, on the other hand, be susceptible to addition at the carbon carbon double bond. The stability of the resulting intermediate may be expected to be somewhat greater than in tetrachloroethylene through resonance stabilization. This would account for acrylonitrile being less stable than either tetrachloroethylene or acetonitrile. Acrylonitrile exhibited the most unusual thermal decomposition behavior of all the compounds tested. It produced a single PIC in very large yield, it had a large fractional reaction order (1.6), and appeared to be concentration dependent.

CONCLUDING REMARKS

At the time of initiation of this program in April 1982, very limited information existed on the thermal decomposition properties of organic compounds commonly subjected to incineration. The existing data discussed in the body of this report, the limited number of studies reviewed in Appendix C, and the data previously generated in our laboratory (15) were not generated on a truly comparable basis. Thus, the development of a scale of hazardous waste incinerability based on experimental data

was virtually impossible. We believe the data generated in this program provides a consistent initial data base for the development of a scale of thermal stability. At a minimum we now have a feeling for the relative stability of a large series of organic compounds and it may be possible to "bracket" the range of the thermal stability of an untested compound.

Clearly, there are many questions which remain to be answered. Our laboratory systems do not exactly simulate an entire incineration system or any zone of an incinerator, so the task remains to model our data to full-scale. However, we feel most strongly that the evaluation of the thermal decomposition properties of hazardous wastes must be performed under well controlled laboratory conditions. Poorly defined and uncontrolled conditions in larger scale units will lead to results which defy intercomparison even by the most experienced scientist or engineer.

We have determined the kinetic relationship of time, temperature, and destruction efficiency for pure compounds decomposing in their own degradation products in air. A logical progression for this work is to study the effect of changing the reaction atmosphere. Controlled studies varying oxygen and water concentrations and introduction of trace species such as NO_x and Cl_2 would allow development of extended kinetic models. We would also envision more detailed studies of the concentration dependence of thermal decomposition rates for selected compounds.

Hazardous waste incinerators are typically used to dispose of waste mixtures. At the direction of EPA's Office of Solid Waste, we have investigated pure compounds. We feel most strongly that investigation of waste mixtures should be a strong part of future research programs. Mixture studies may be conducted by two methods: doping the compound of interest into a standard mixture or investigation of individual waste mixtures. Mixture studies should be complemented by controlled kinetic studies to facilitate mechanistic and kinetic model development.

The preliminary calculations presented in the text indicate that "fault" modes of the incinerator, or equivalently the extremes of the parameter distribution functions, may well control measured incineration efficiency for full-scale units. Following this line of reasoning, one would logically conclude that the incinerator effluent would only contain undecomposed feed material and products of incomplete combustion which were formed under these conditions of failure. From a strictly environmental viewpoint we are interested in what is being emitted from the incinerator with less emphasis on mechanisms of destruction, although the two topics are clearly related. The point is that the "fault" modes are essentially worst case conditions and appear to have a dominating effect on the composition of the incinerator effluent. For this reason, we feel that the majority of future studies should be conducted under these failure conditions. Although these conditions are not presently well-defined, an atmosphere containing 1% oxygen and a residence time of 0.25 seconds might be considered representative.

A further point to be made along this vein is that the temperature at which our studies are conducted are representative of fault modes. Our experimental temperature range is designated to cover 0 to 99.9% destruction of the feed material and is typically several hundred degrees below mean temperatures quoted for hazardous waste incineration. If a given incinerator does not meet the 99.99% destruction efficiency requirement, yet has a high mean operating temperature, then a likely possibility for its failure is that a fraction of the waste feed experiences temperatures somewhat lower than the mean where destruction efficiency is low, i.e., the destruction efficiency and temperature range measured in our laboratory studies.

Thus, one might expect the actual PICs emitted from the incinerator to be the same as those formed under the conditions studied in the laboratory. Furthermore, this reasoning suggests

that the relative thermal stability of hazardous wastes should be compared at fault mode temperature since only this fraction of the waste is escaping incineration. Since selecting a suitable temperature for comparison of every compound is difficult and still somewhat arbitrary, we would suggest a ranking based on the temperature required for 99% destruction at 2 seconds mean residence time. One could just as well select 90% or 99.9%, but examination of the data shows that the rankings over this range are essentially identical.

In any case, it is clear what should not be done. The compounds should not be ranked at a high temperature where all of the compounds would be essentially totally destroyed since the waste fraction experiencing this temperature in an incinerator would have no effect on the composition of the incinerator effluent.

Our research has addressed non-flame, high-temperature, gas phase reaction chemistry. We have not as yet directly addressed so-called flame-mode chemistry or physical phenomena such as heat and mass transport. Heat and mass transport effects may have significant impact on incineration efficiency by, for example, controlling condensed phase vaporization rates and gas phase mixing rates. We would suggest that experimental programs be designed to isolate these parameters as opposed to attempting to lump them into bench, pilot, or full-scale studies which would be poorly controlled.

Flame mode studies represent a special challenge due to the difficulties in scaling results. Of all incineration processes which must be modeled to full-scale, gas phase chemical kinetics is the easiest and most successfully performed. The temporal and spatial distributions present in small laboratory or bench-scale flames are not easily scaled to the turbulent poorly-defined flames present in full-scale systems. Consequently, we would suggest a kinetic approach to determining flame mode destruction efficiencies.

The importance of hydroxyl radicals in flames is well documented. (31,32) Thus, an experimental program to determine the rate of attack of hydroxyl radical on hazardous wastes would produce kinetic results which is easily scaled. Kinetic data of this type in combination with measurement or estimation of hydroxyl radical concentrations in full-scale systems would allow simple scaling of laboratory results to full-scale. These data over different temperature ranges would be applicable to both flame and non-flame modes of destruction.

Products of incomplete combustion have not been considered in this report. PIC determination would remove much of the speculation in our discussion of reaction mechanisms. In previous research we have observed the formation of numerous PICs from a wide variety of organic compounds. These PICs have, in some cases, been produced in as much as 50% yields and been as hazardous or more hazardous than the parent compound. (6,7,15). We feel that determination of PICs should be an integral part of future research plans and an integral part of any successful ranking of incinerability.

We anticipate that our own research will include increased activity in this area. A collaborative program with Professor Christoffer Rappe of the University of Umeå has been initiated to study the possible formation of chlorinated dibenzodioxins and dibenzofurans from the controlled thermal degradation of chlorinated organics. This will complement our ongoing work on PIC identification.

Many ongoing questions can be addressed when the US-EPA's Combustion Research Facility in Jefferson, Arkansas begins studies of incineration of hazardous wastes in early 1984. This facility will allow testing at the pilot-scale of many of the concepts proposed by various research groups. Four proposed rankings of incinerability have been discussed in this report, and other methods have been recently proposed based on flame studies and ignition delay times. (33,34) A round-robin test program of actual waste samples by each ranking method with the

output being a prediction of the major organic constituents (both POHCs and PICs) of the stack effluent when these wastes are incinerated should prove to be a most valuable study. The results of incineration of the waste at the Combustion Research Facility could be used as the basis for comparison of the predictions of the various ranking schemes.

In the planning of future research in the area of incineration, three general areas of research may be defined. One area would be research aimed at gaining a basic understanding of the incineration process. A second would be development of a data base for addressing already acknowledged environmental concerns. The third would be to identify potentially serious environmental questions as yet undiscovered. The first and third areas would be long term while the second must be addressed rapidly and on a continuing basis. A proper balance of emphasis on these research areas is essential to the long-term development and understanding of incineration.

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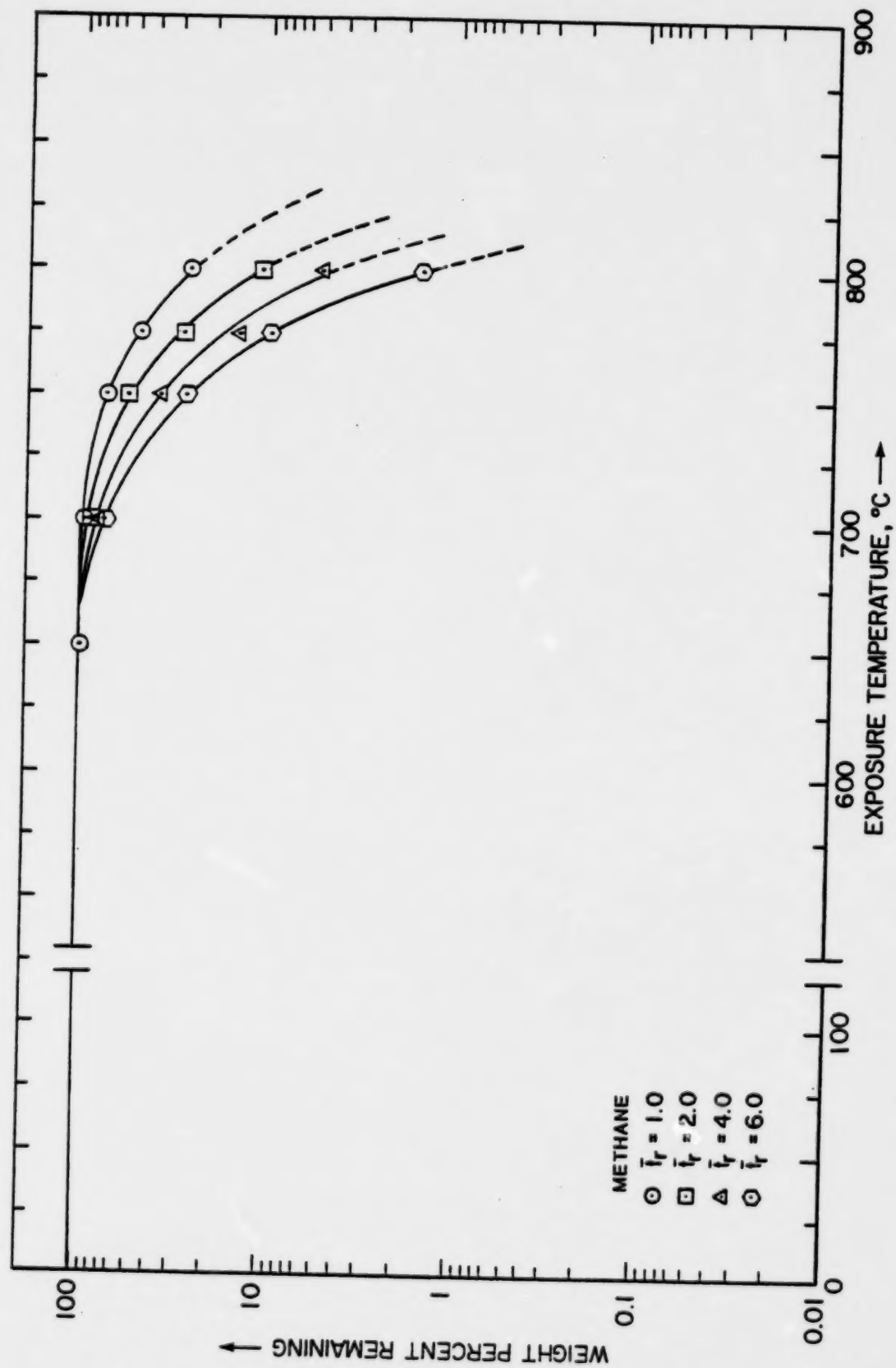
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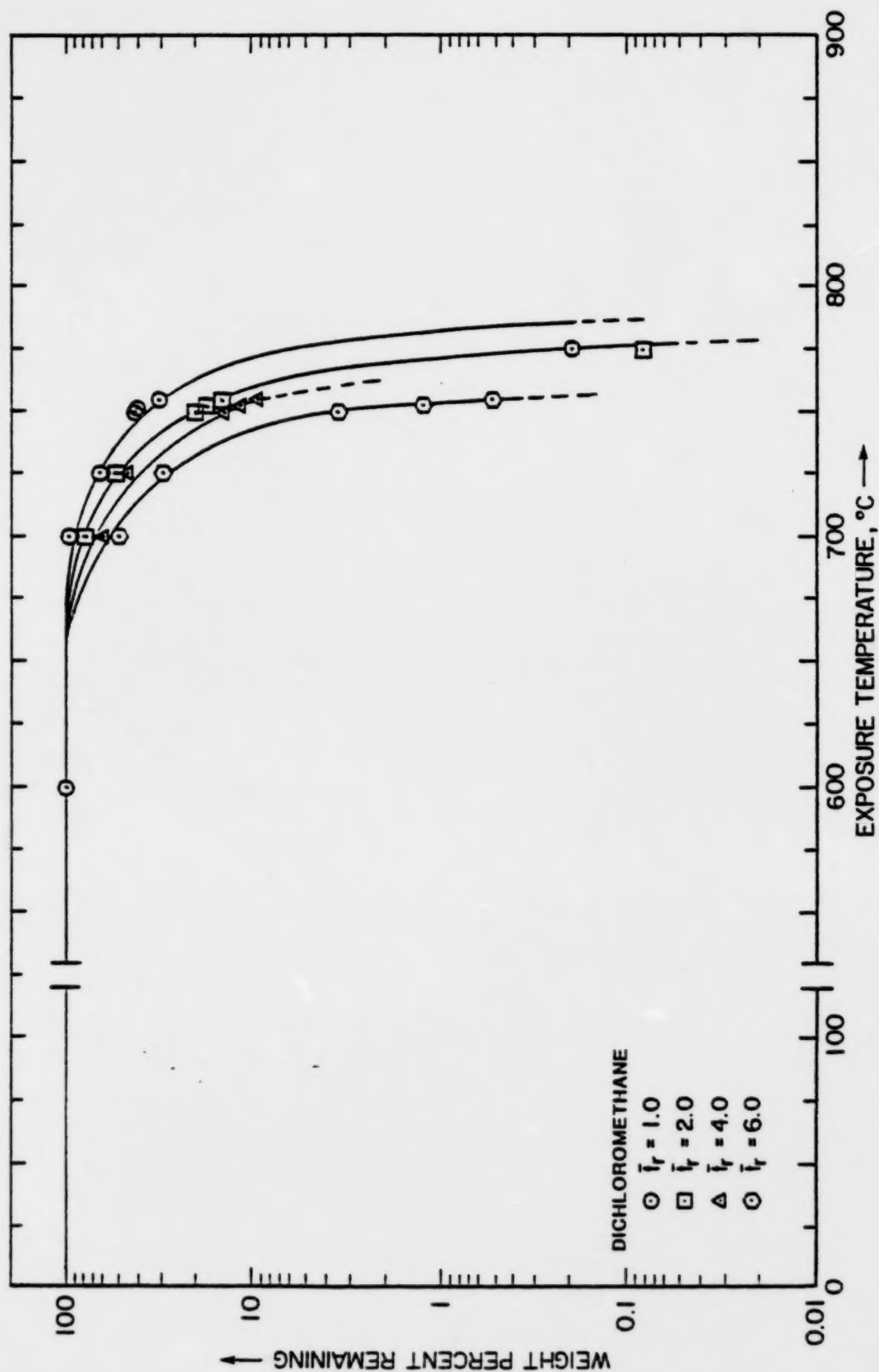
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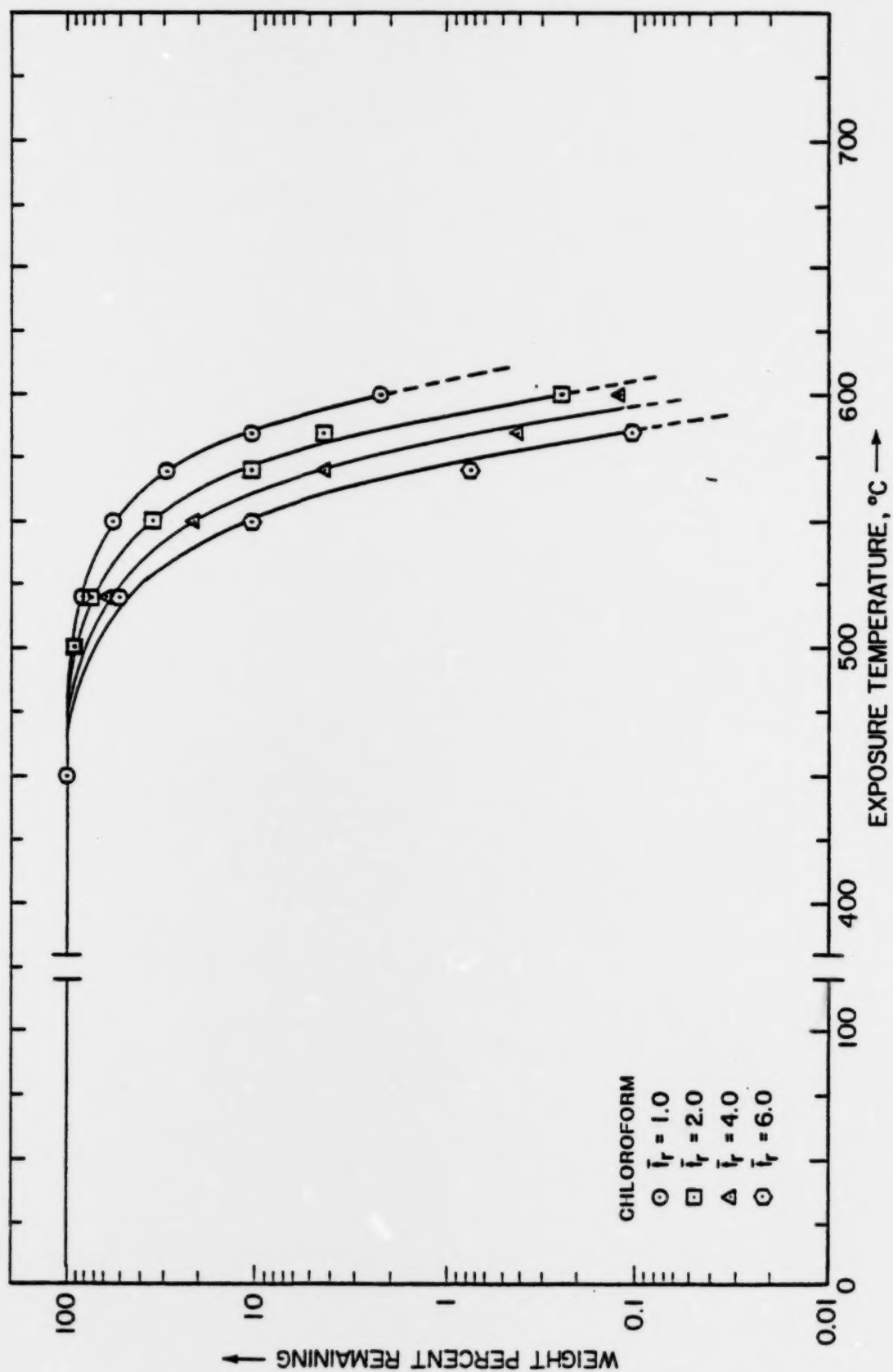
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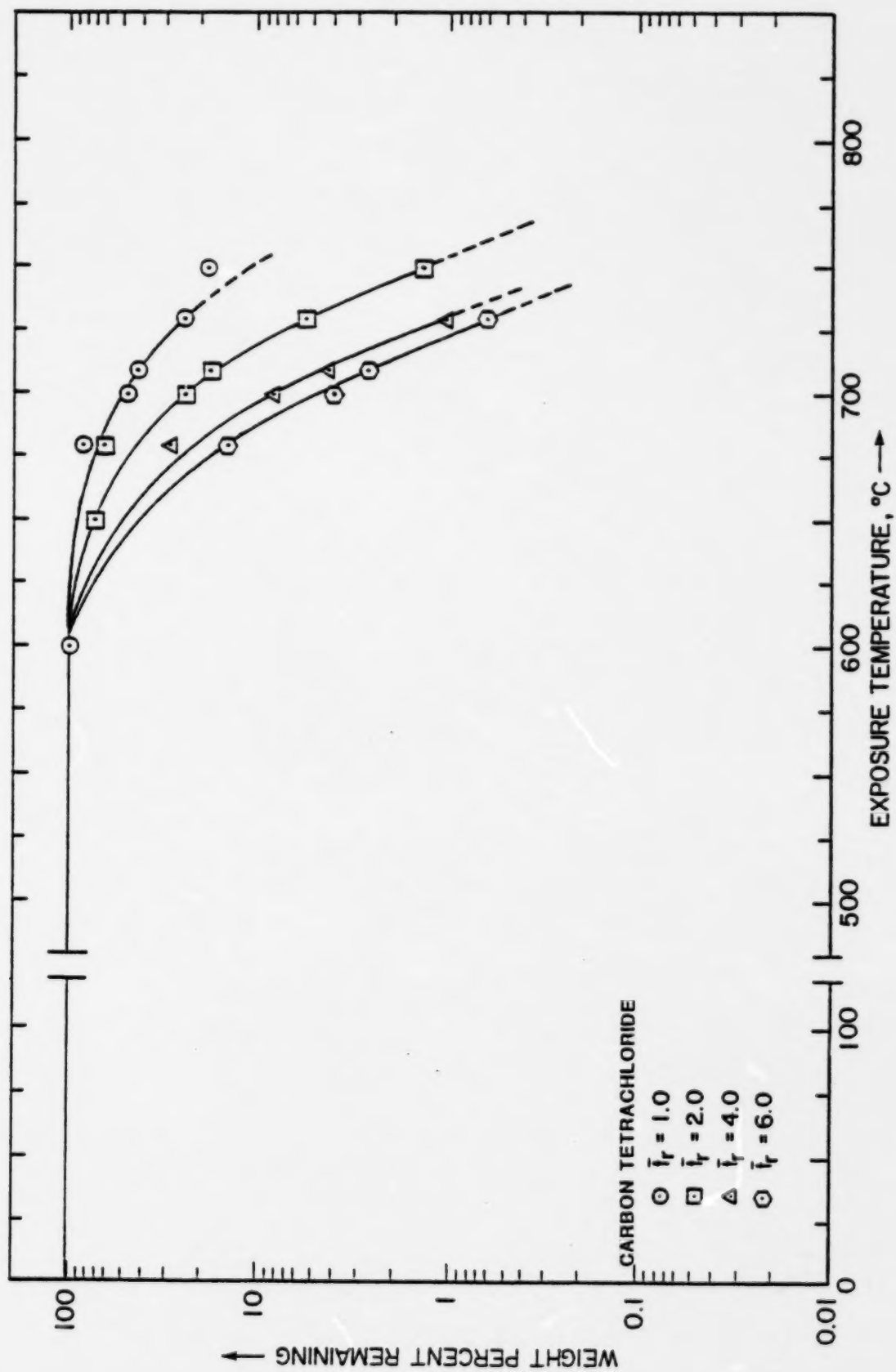
APPENDICES

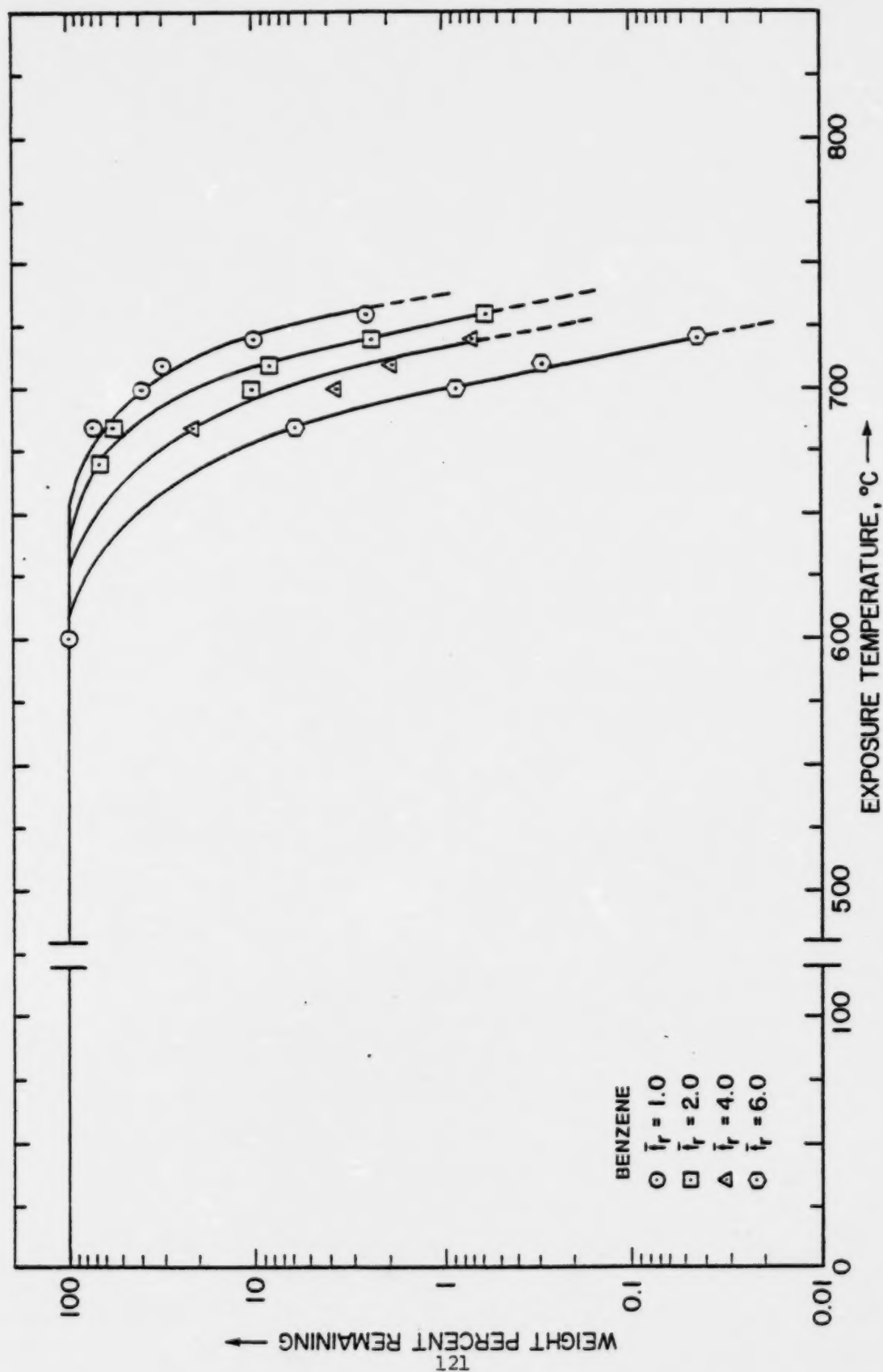
APPENDIX A
THERMAL DECOMPOSITION PROFILES

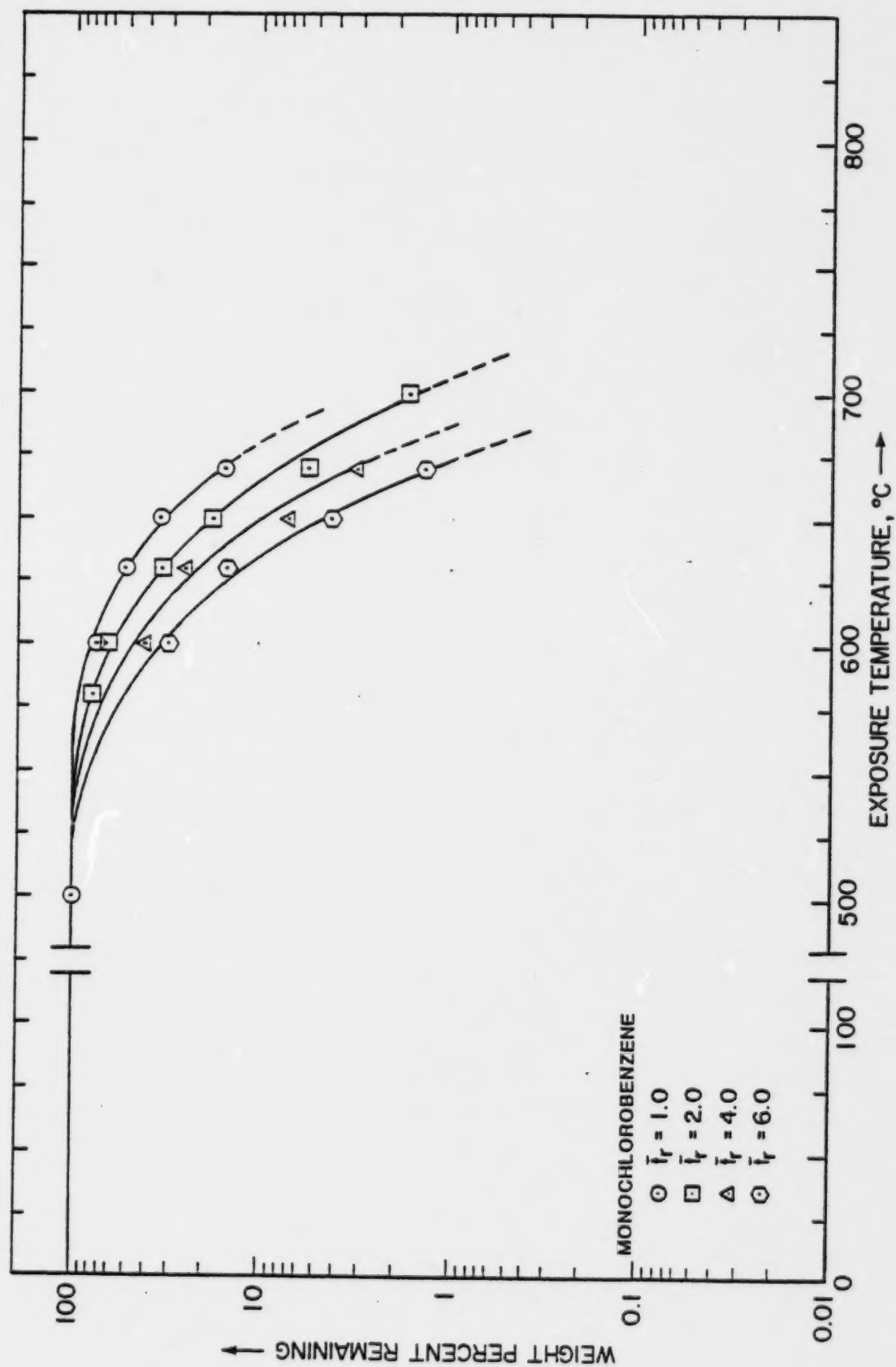


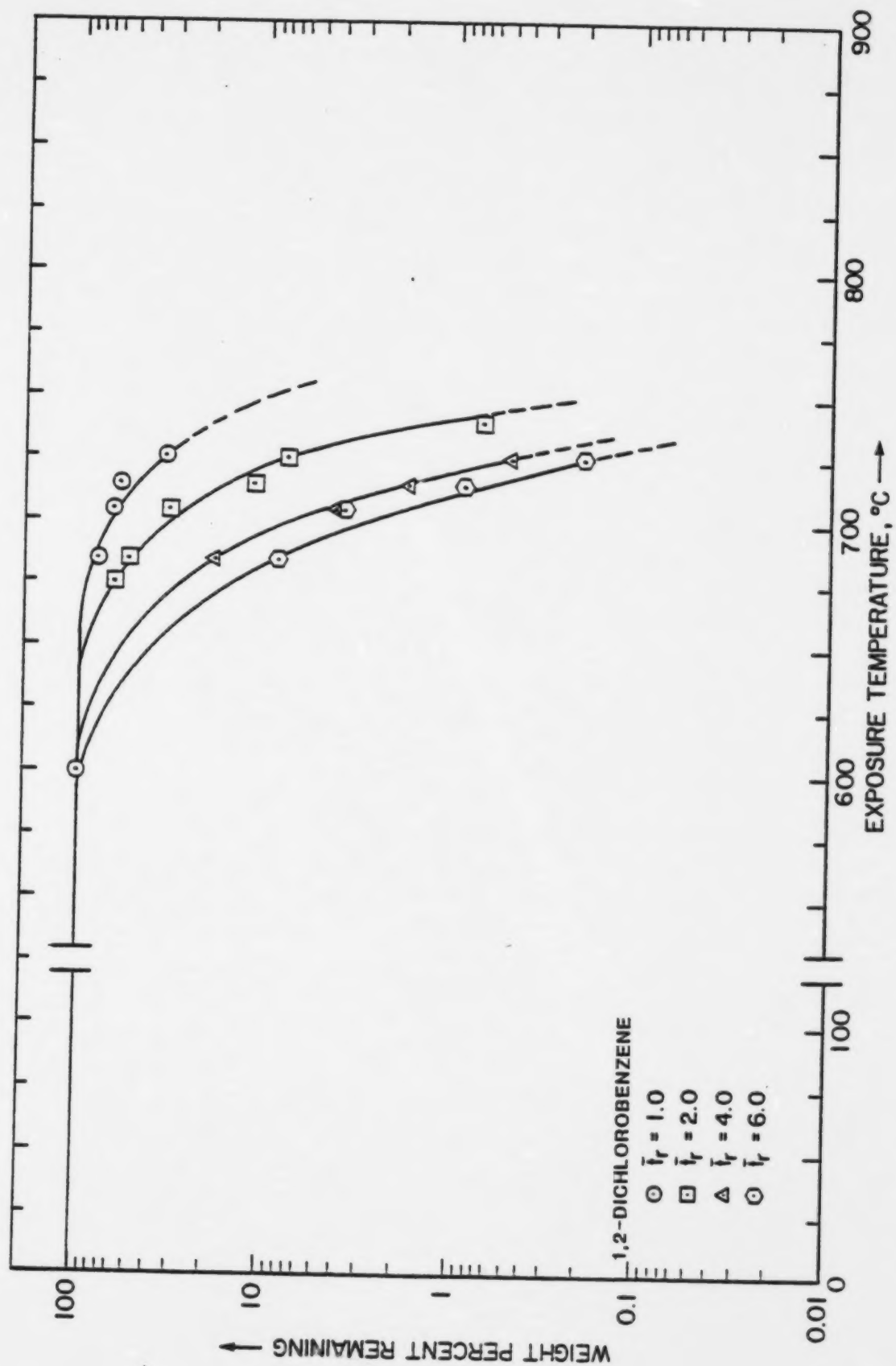


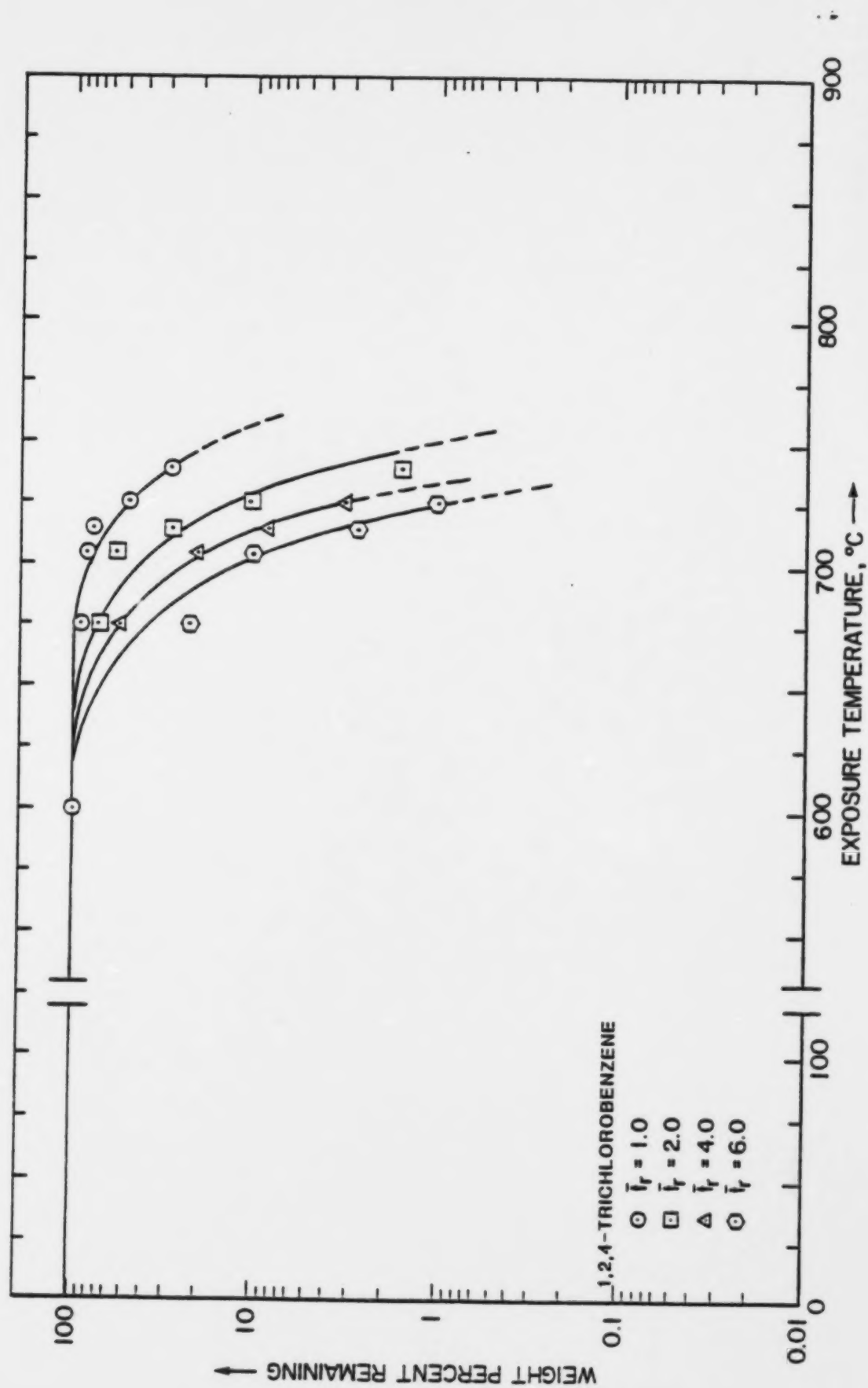


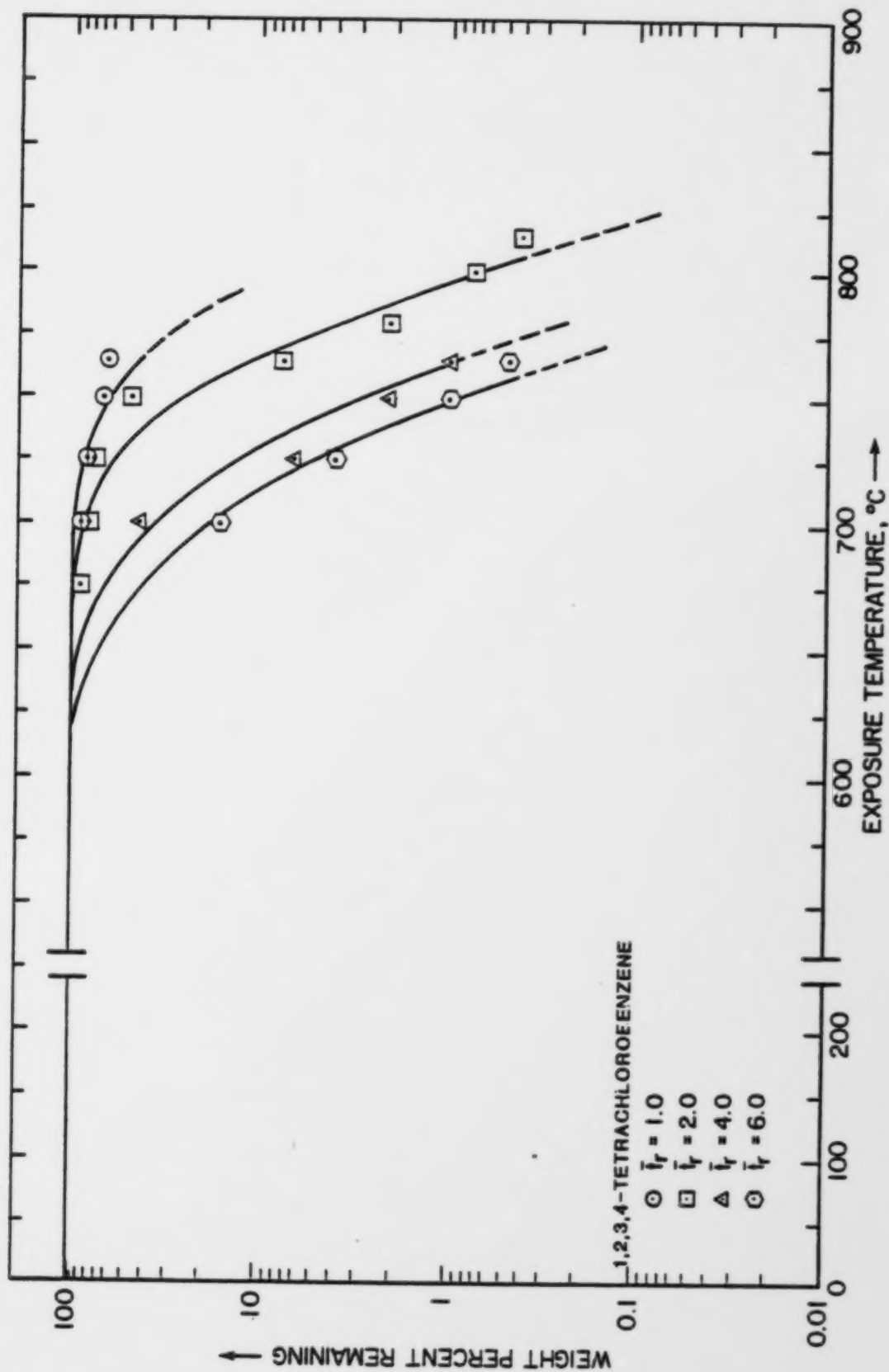


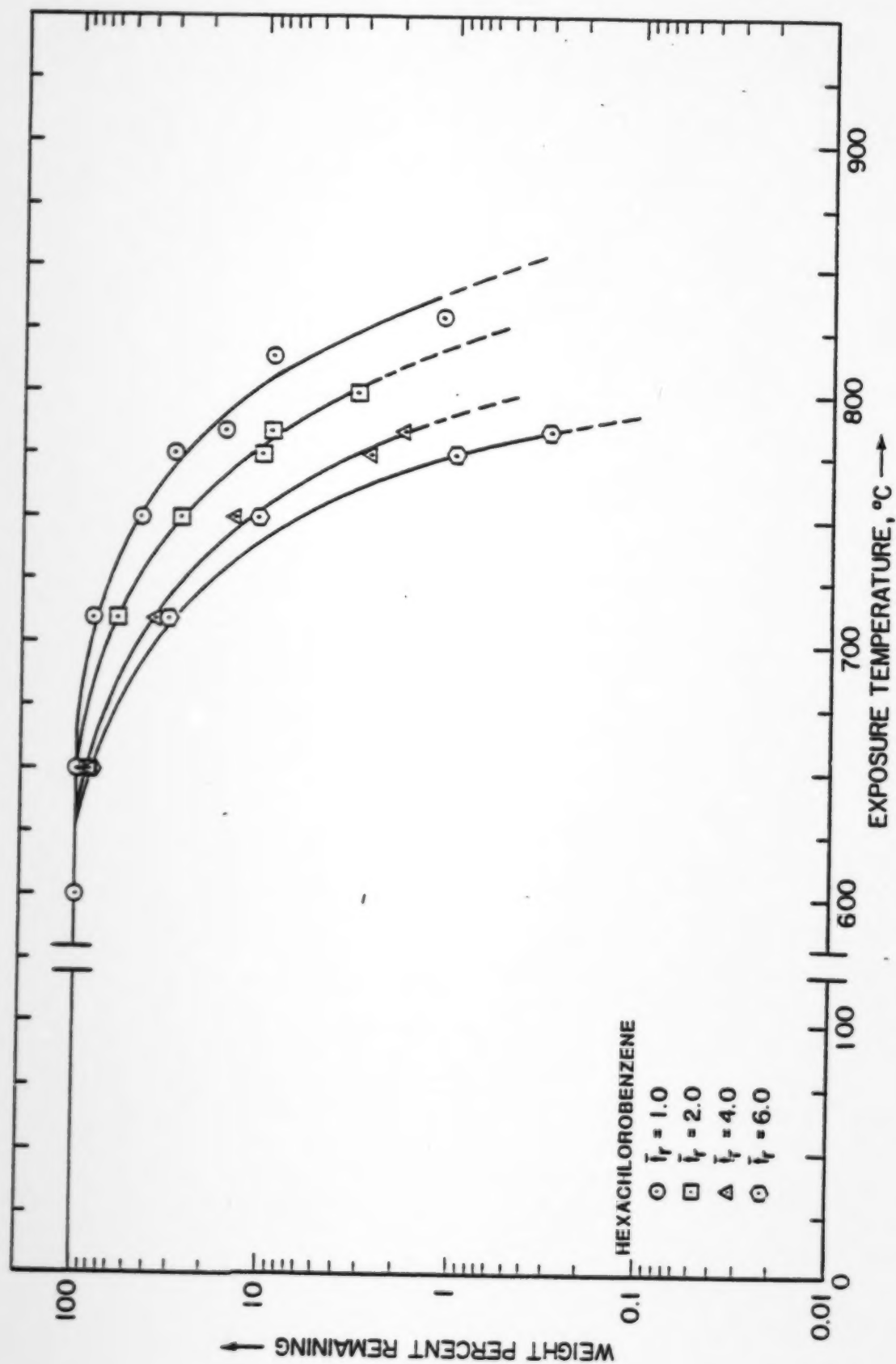


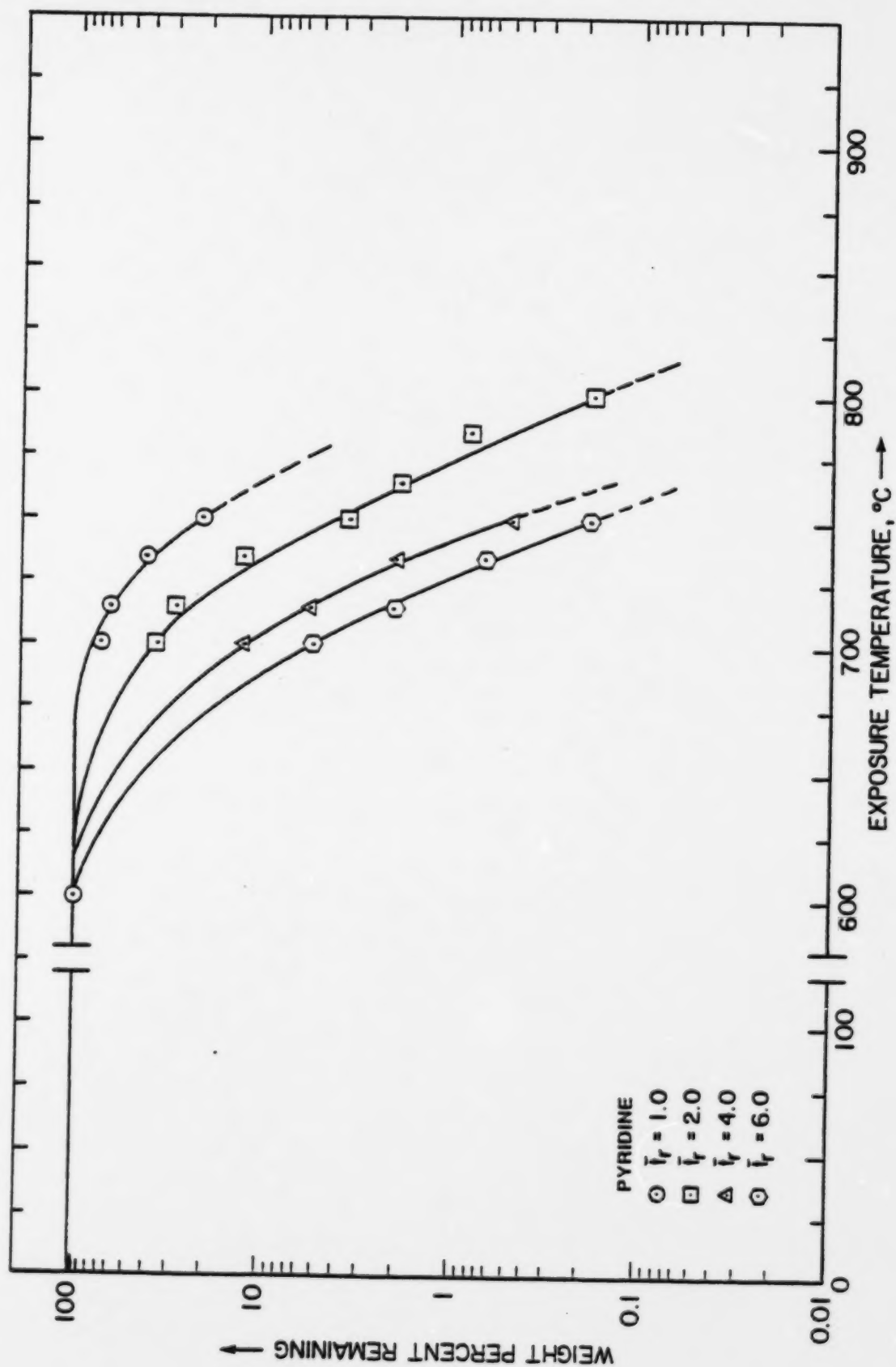


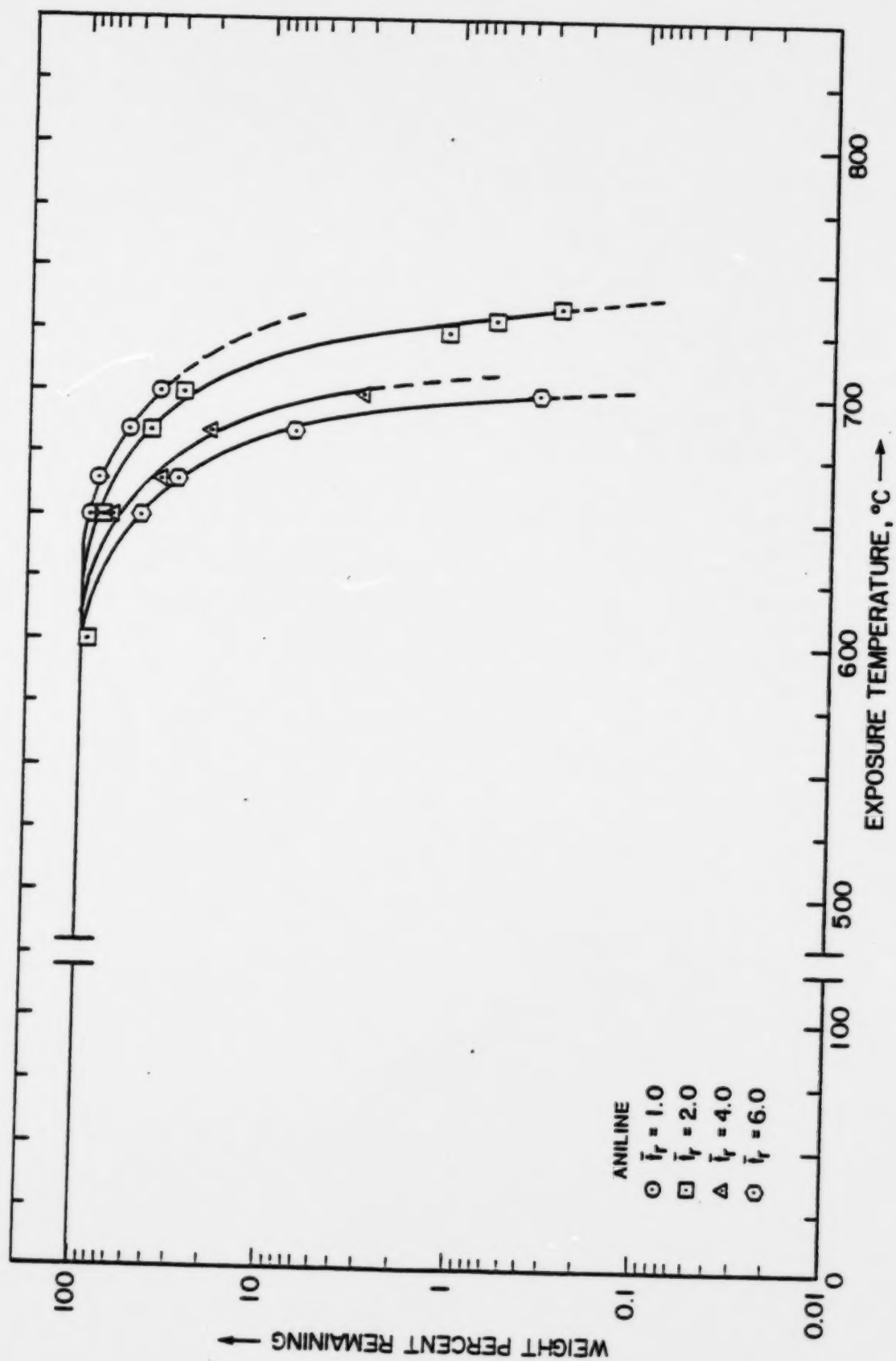


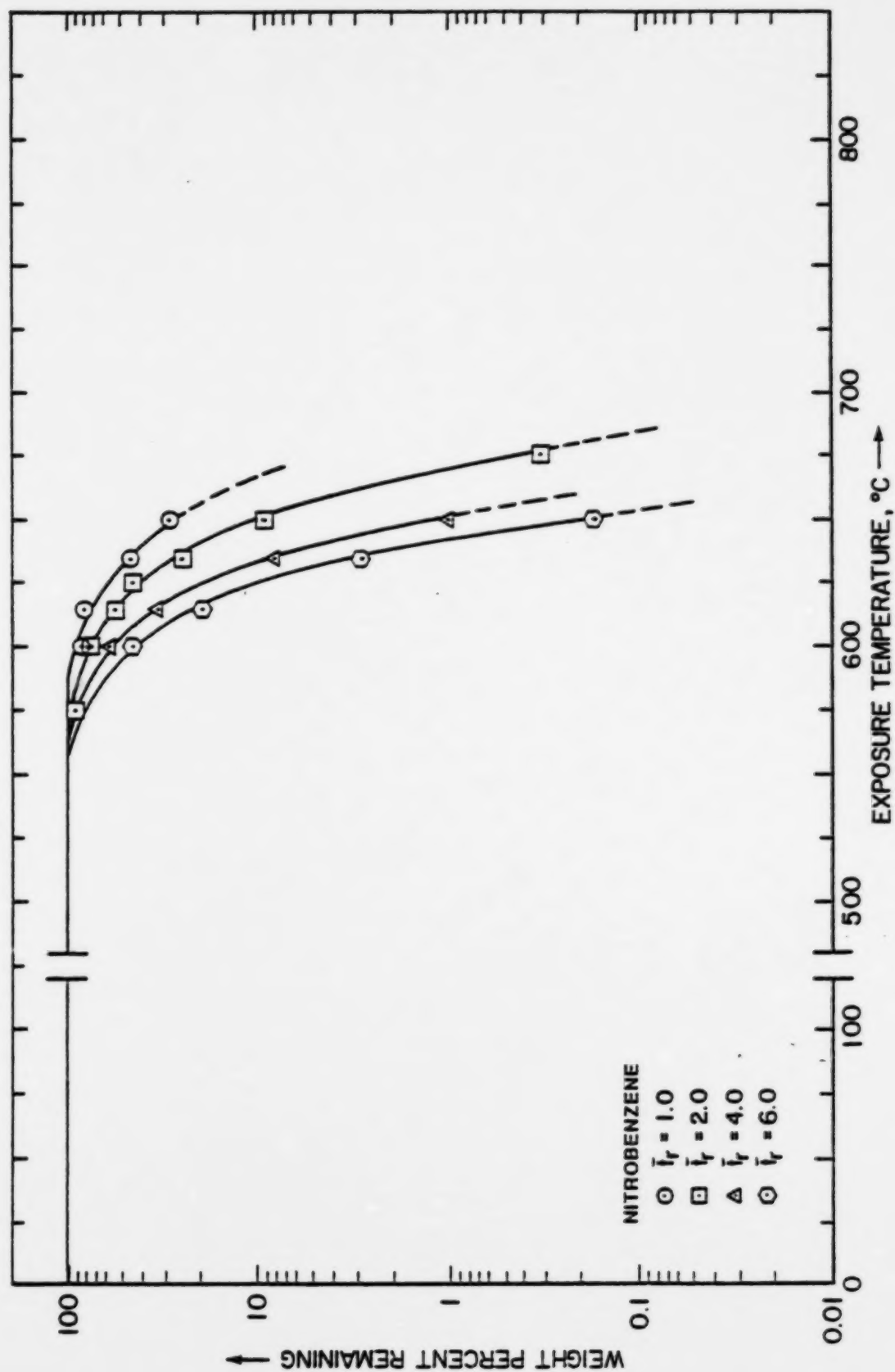


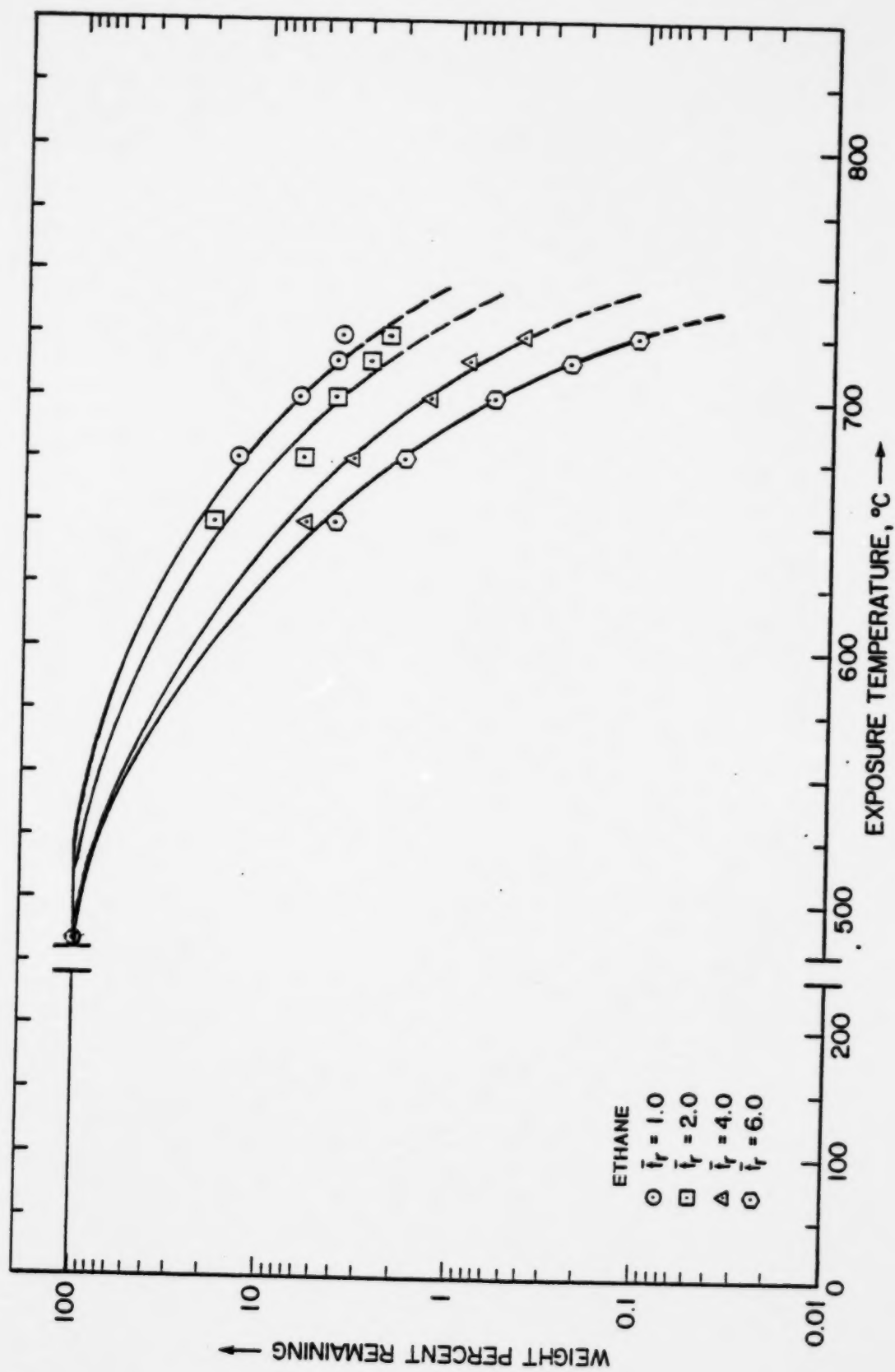


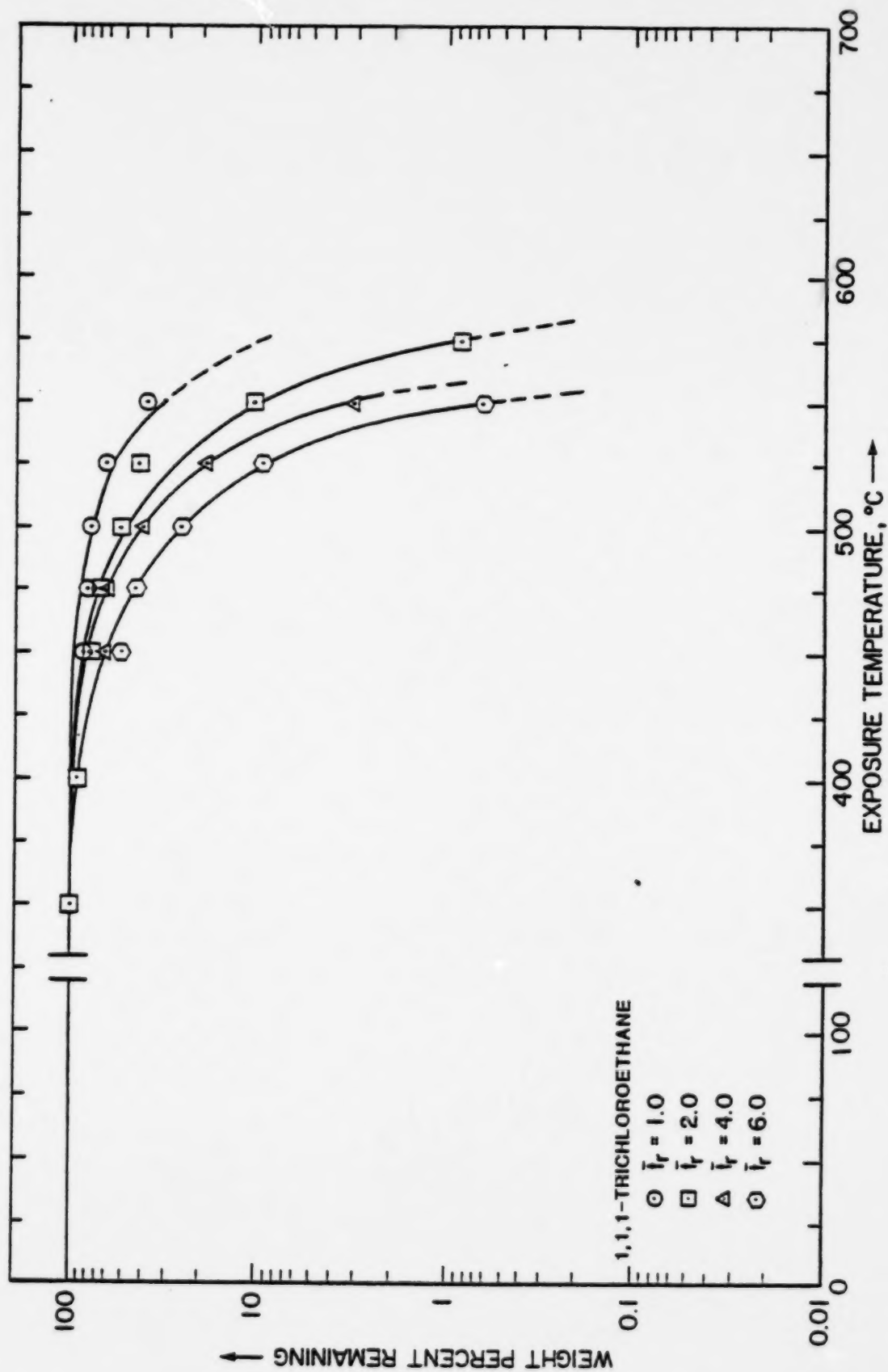


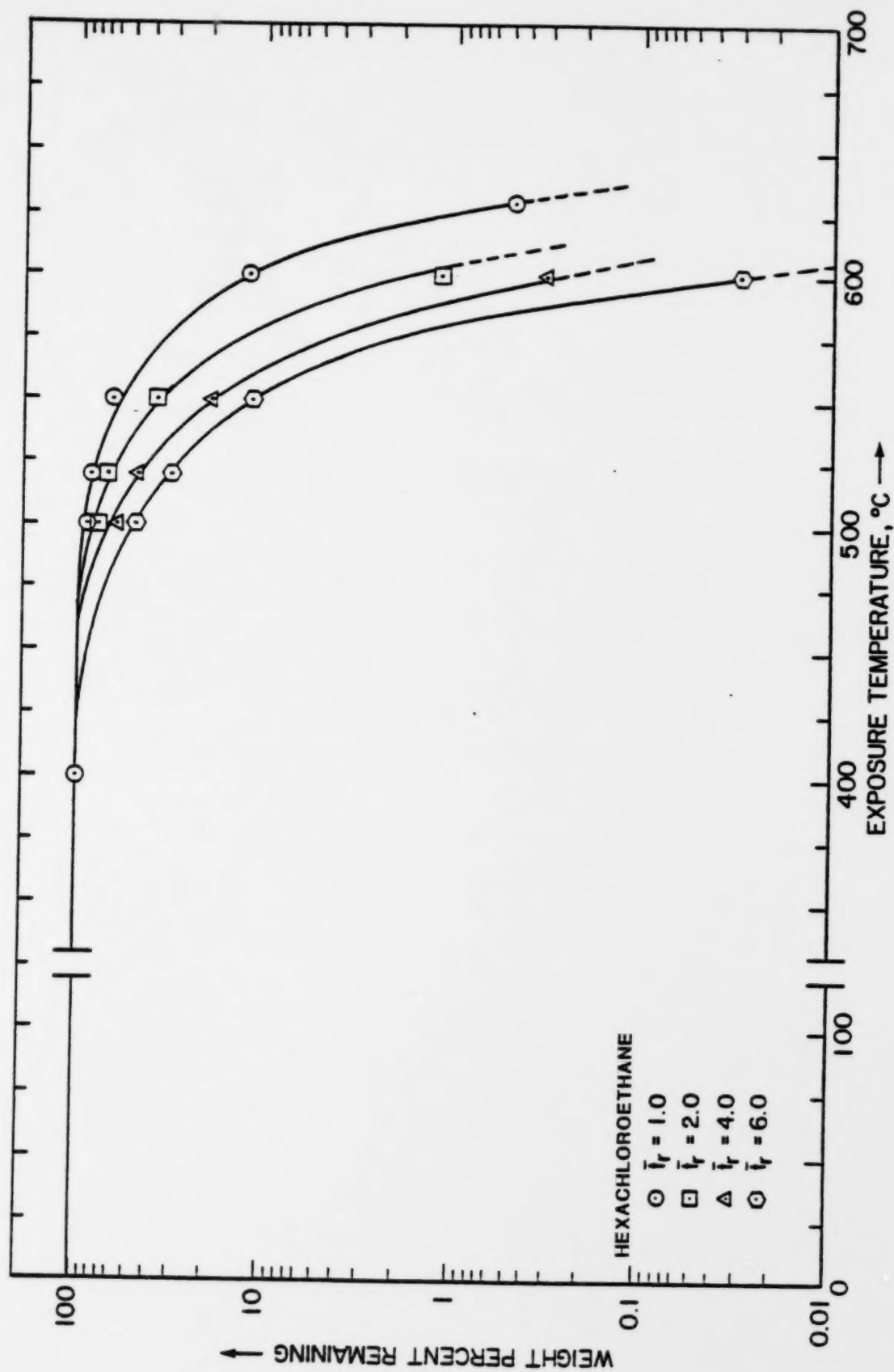


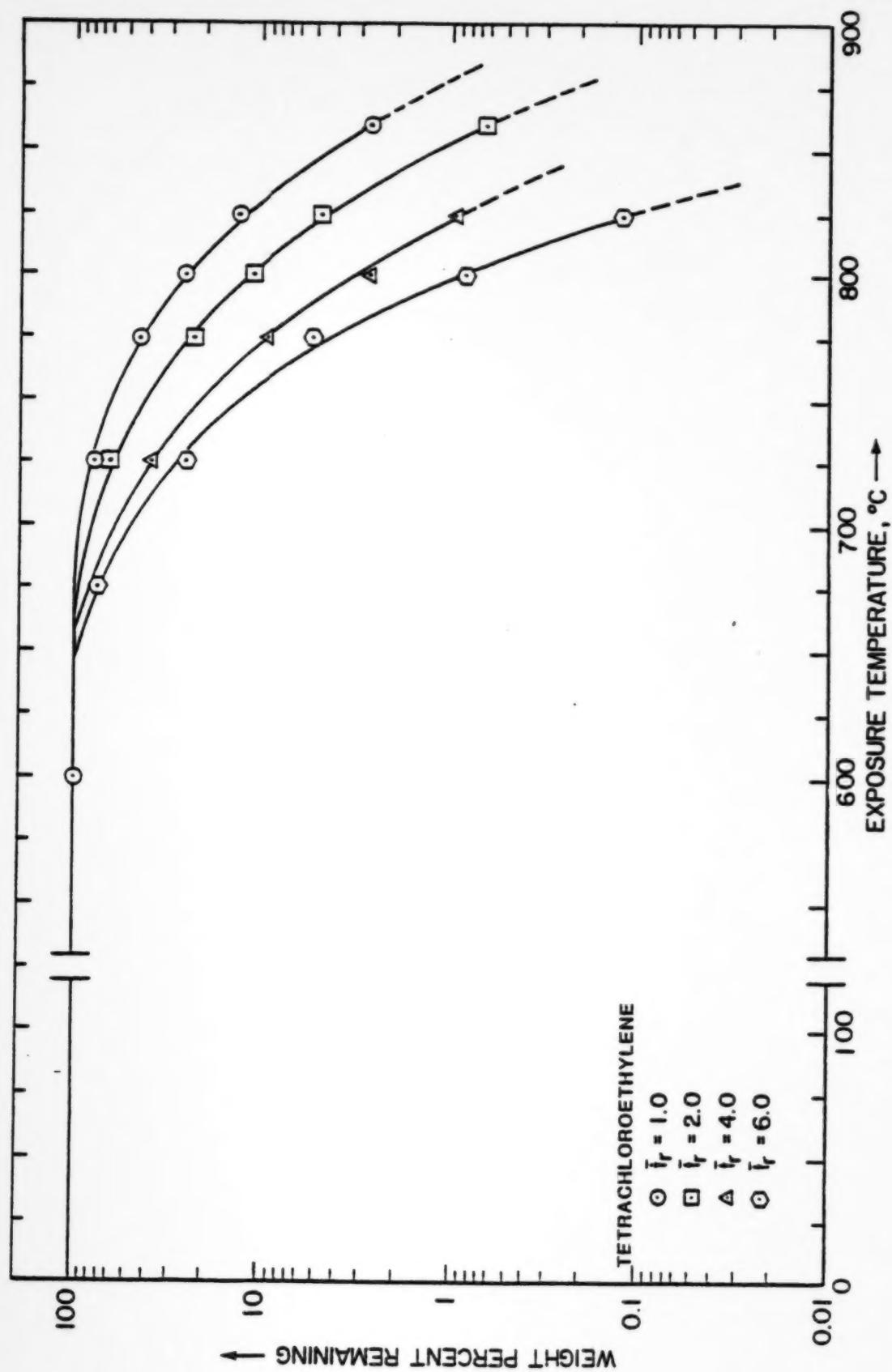


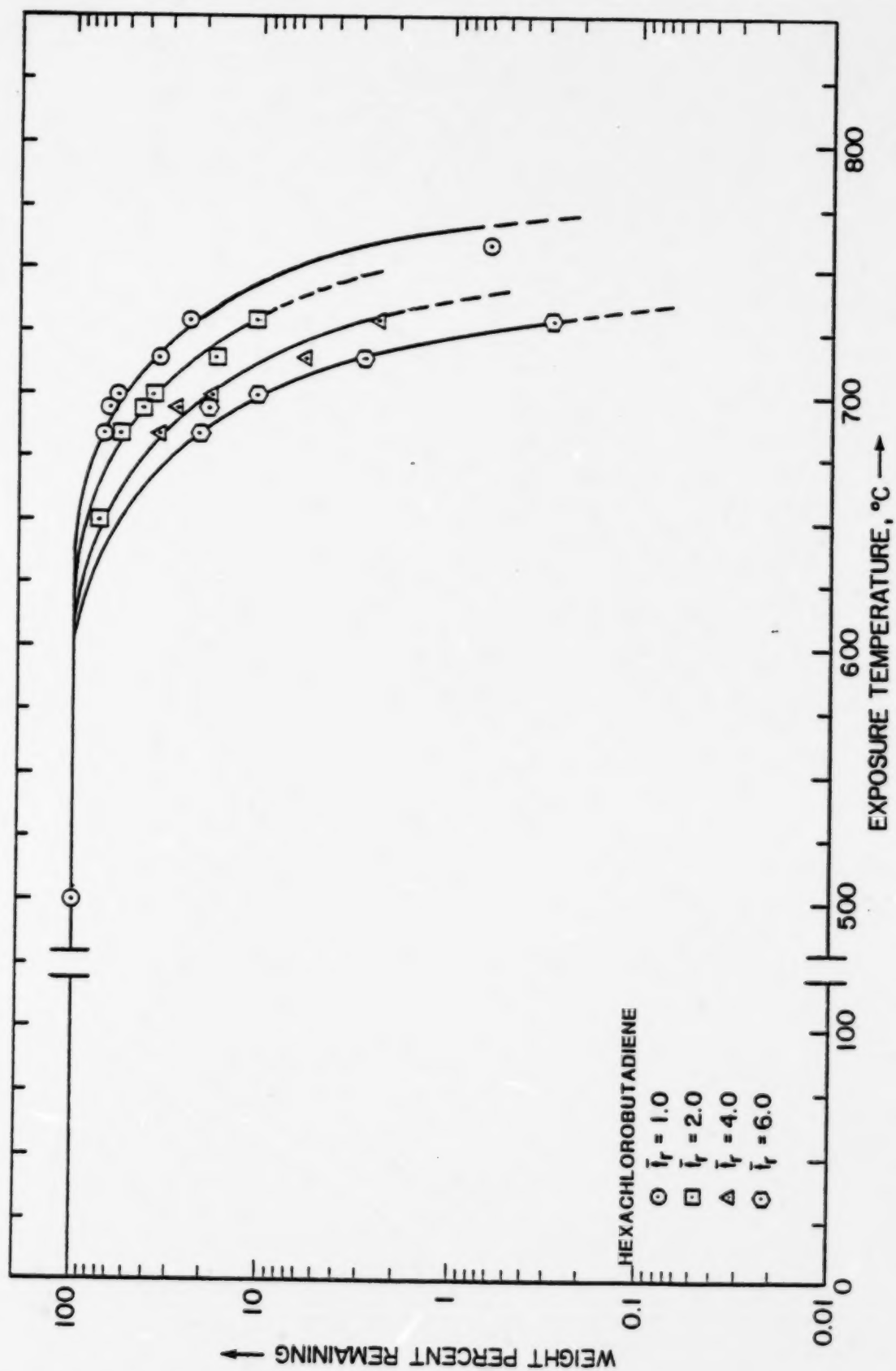


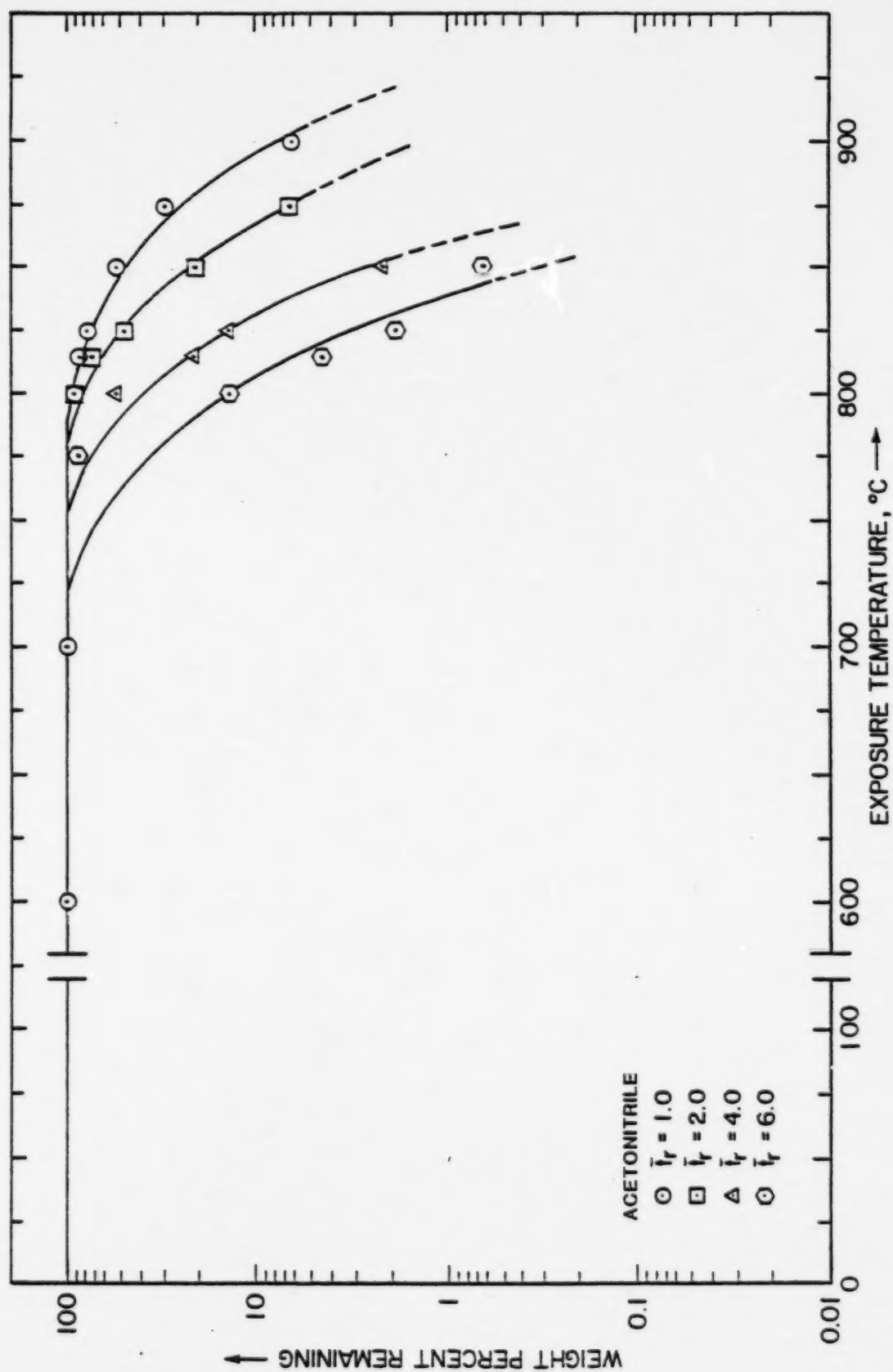


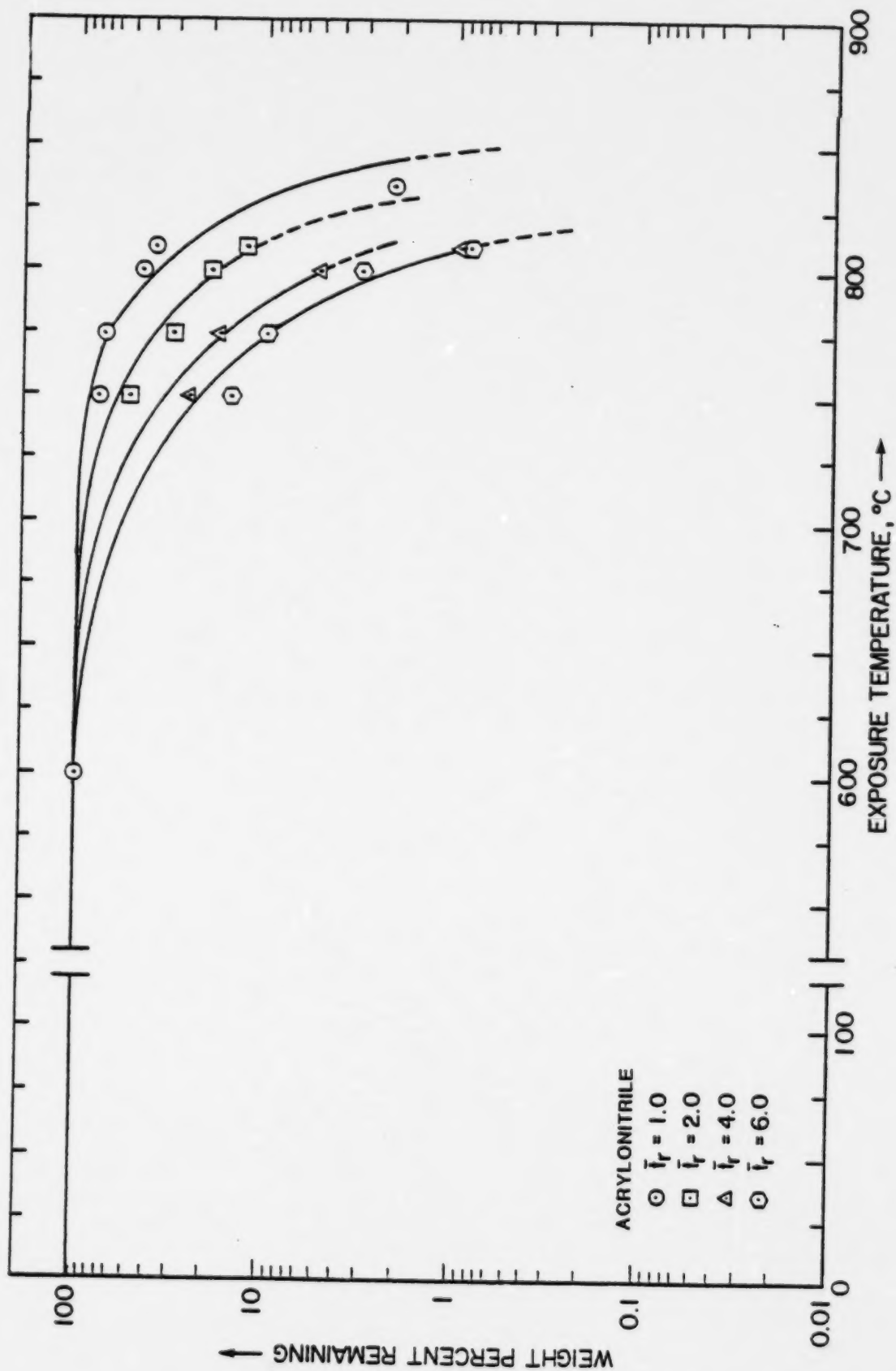












APPENDIX B
KINETIC DATA SUMMARIES

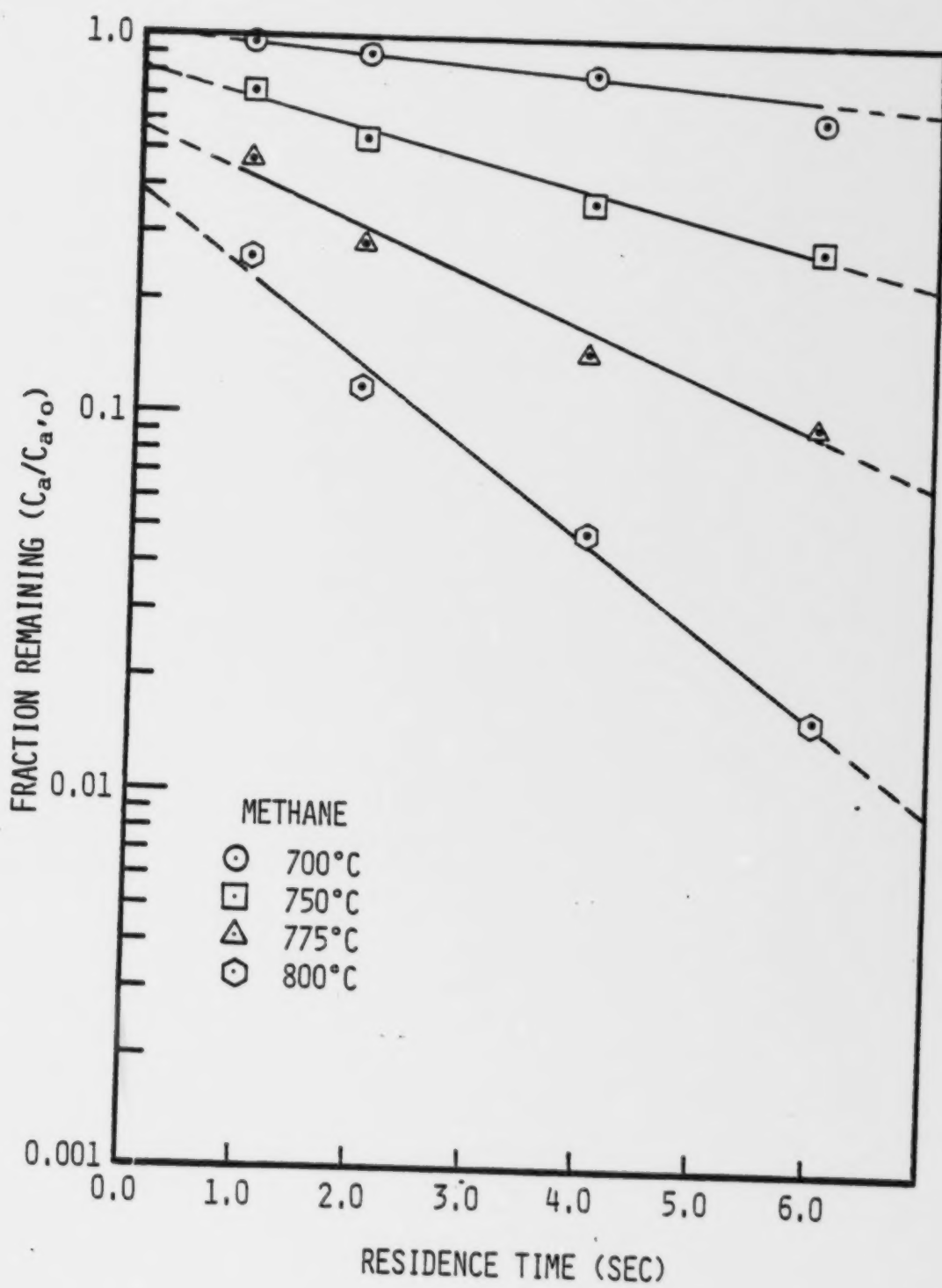
METHANE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	550	650	700	750	775	800	
1.0	100	100	97.8	73.6	48.0	26.6	
2.0			91.3	55.0	29.2	11.6	
4.0			84.0	37.6	15.2	5.04	
6.0	100	100	74.5	28.3	9.94	1.58	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
700	0.053	0.99
750	0.188	0.98
775	0.310	0.97
800	0.541	0.99
$E_a = 48 \text{ kcal/mole}$ $r^2 = 1.00$ $A = 3.5 \times 10^9 \text{ sec}^{-1}$		

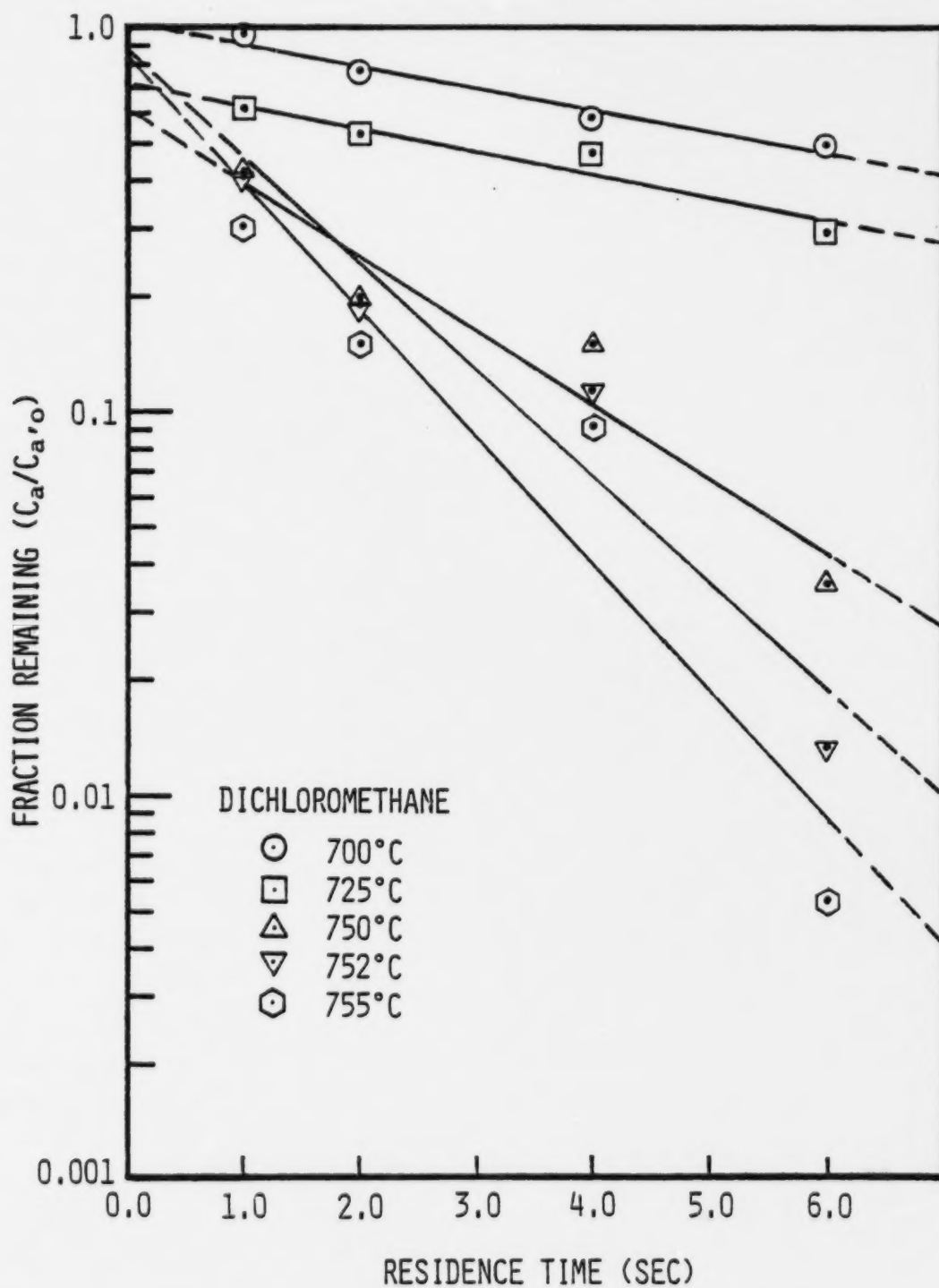


DICHLOROMETHANE
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	700	725	750	752	755	775
1.0	100	99.0	63.6	41.6	40.99	31.4	0.19
2.0	100	79.0	52.3	20.0	19.0	14.4	0.08
4.0	100	59.6	47.1	14.2	11.8	9.25	
6.0	100	50.0	29.6	3.55	1.3	0.53	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
700	0.134	0.97
725	0.141	0.93
750	0.451	0.94
752	0.642	0.92
755	0.757	0.89
$E_a = 64 \text{ kcal/mole}$ $r^2 = 0.85$ $A = 3.13 \times 10^{13} \text{ sec}^{-1}$		

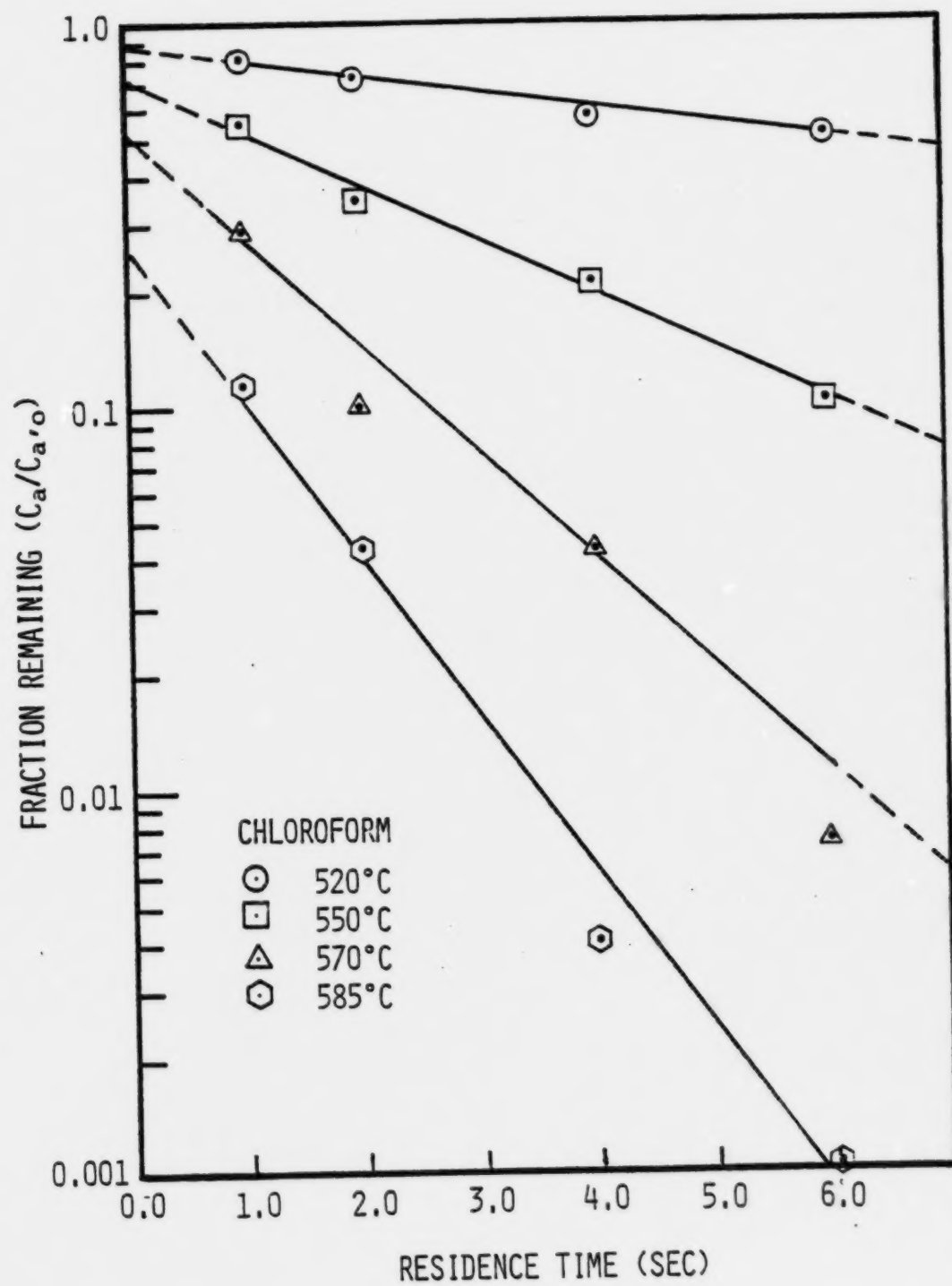


CHLOROFORM
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	400	500	520	550	570	585	600
1.0	100		81.2	55.7	29.3	11.2	2.29
2.0	100	86.0	74.4	34.8	10.3	4.29	0.24
4.0	100		58.5	21.3	4.27	0.41	0.13
6.0	100		51.0	10.4	0.75	0.108	>0.03

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
520	0.096	0.99
550	0.322	0.99
570	0.693	0.98
585	0.952	0.99
$E_a = 49 \text{ kcal/mole}$ $r^2 = 0.99$ $A = 2.9 \times 10^{12} \text{ sec}^{-1}$		

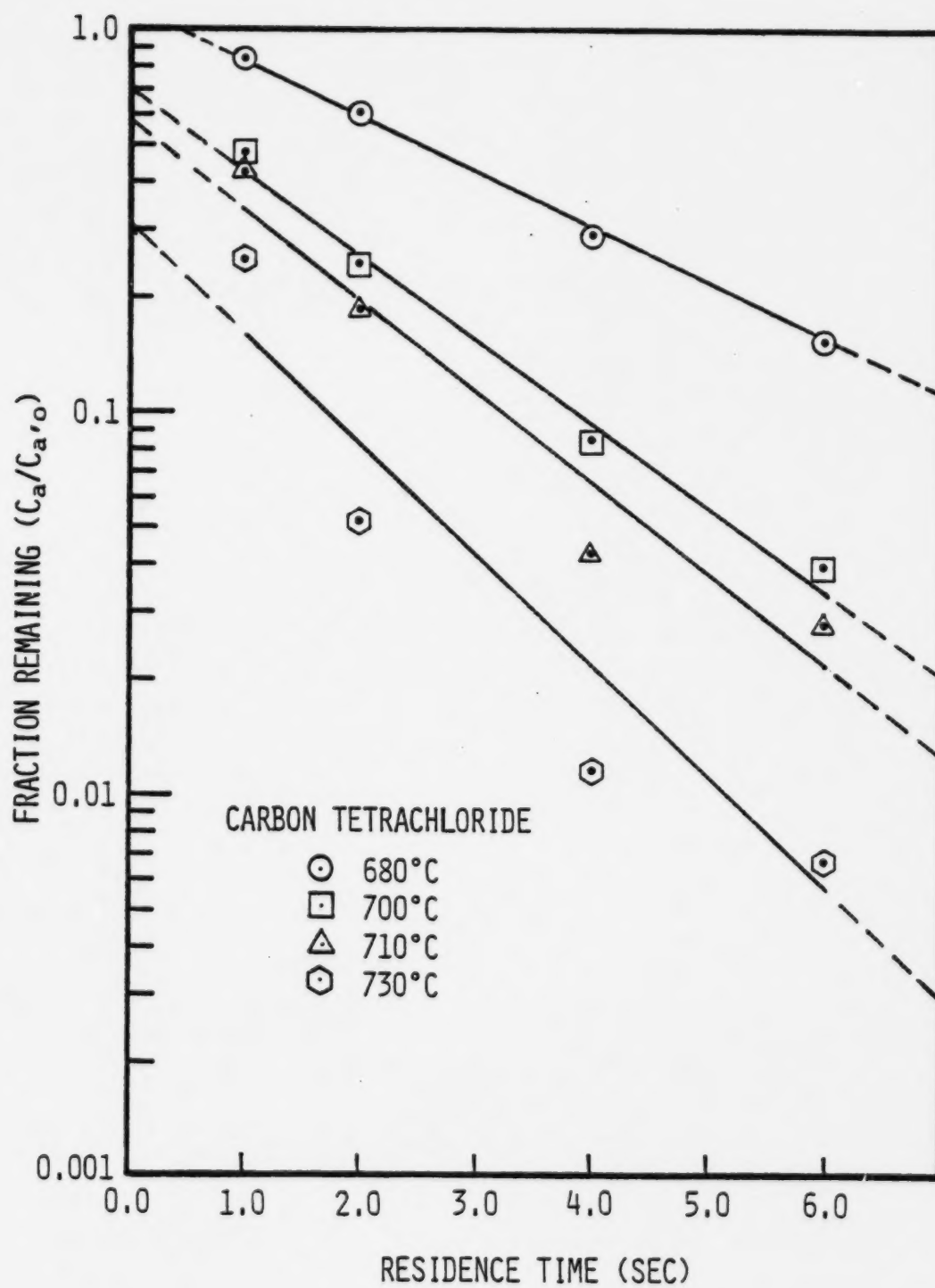


CARBON TETRACHLORIDE
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time t_r (s)	Exposure Temperature $T(^{\circ}\text{C})$						
	600	650	680	700	710	730	750
1.0	100		86.4	48.2	43.4	24.9	19.2
2.0	100	72.7	62.3	24.3	18.1	5.51	1.46
4.0	100		29.5	8.46	4.27	1.14	
6.0	100		14.9	4.00	2.80	0.68	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}\text{C})$	Rate Constant k_1 (s^{-1})	Correlation Coefficient r^2
680	0.355	1.00
700	0.494	0.99
710	0.555	0.94
730	0.700	0.91
$E_a = 26 \text{ kcal/mole}$ $r^2 = 0.99$ $A = 2.8 \times 10^5 \text{ sec}^{-1}$		



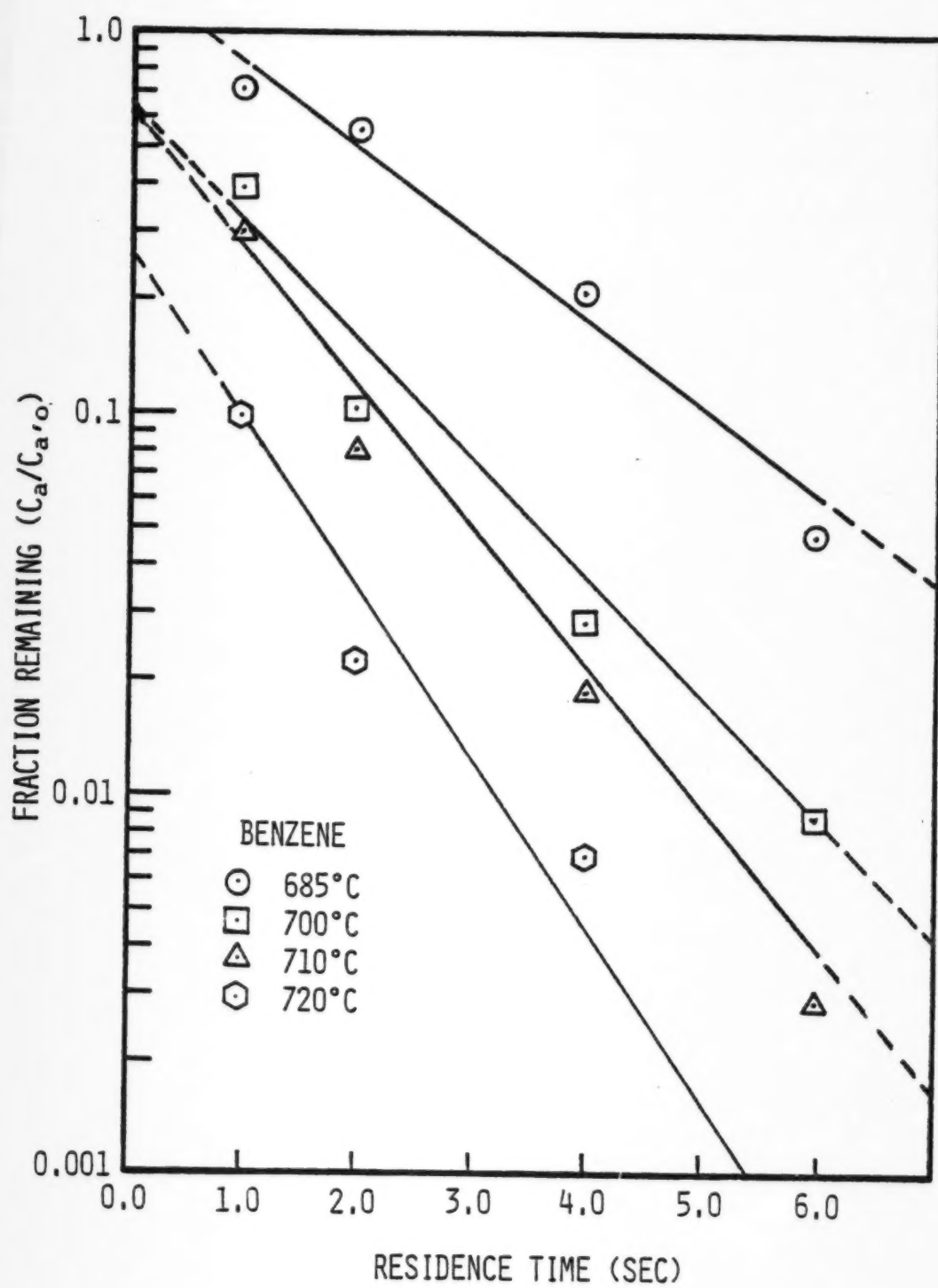
BENZENE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	670	685	700	710	720	730
1.0	100		72.4	39.8	30.6	9.86	2.60
2.0	100	64.5	55.1	10.2	8.18	2.34	0.58
4.0	100		21.0	3.66	1.86	0.70	
6.0	100		5.80	0.87	0.287	0.04	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
685	0.510	0.98
700	0.719	0.97
710	0.901	0.99
720	1.03	0.97
$E_a = 38 \text{ kcal/mole}$ $r^2 = 0.99$ $A = 2.8 \times 10^8 \text{ sec}^{-1}$		



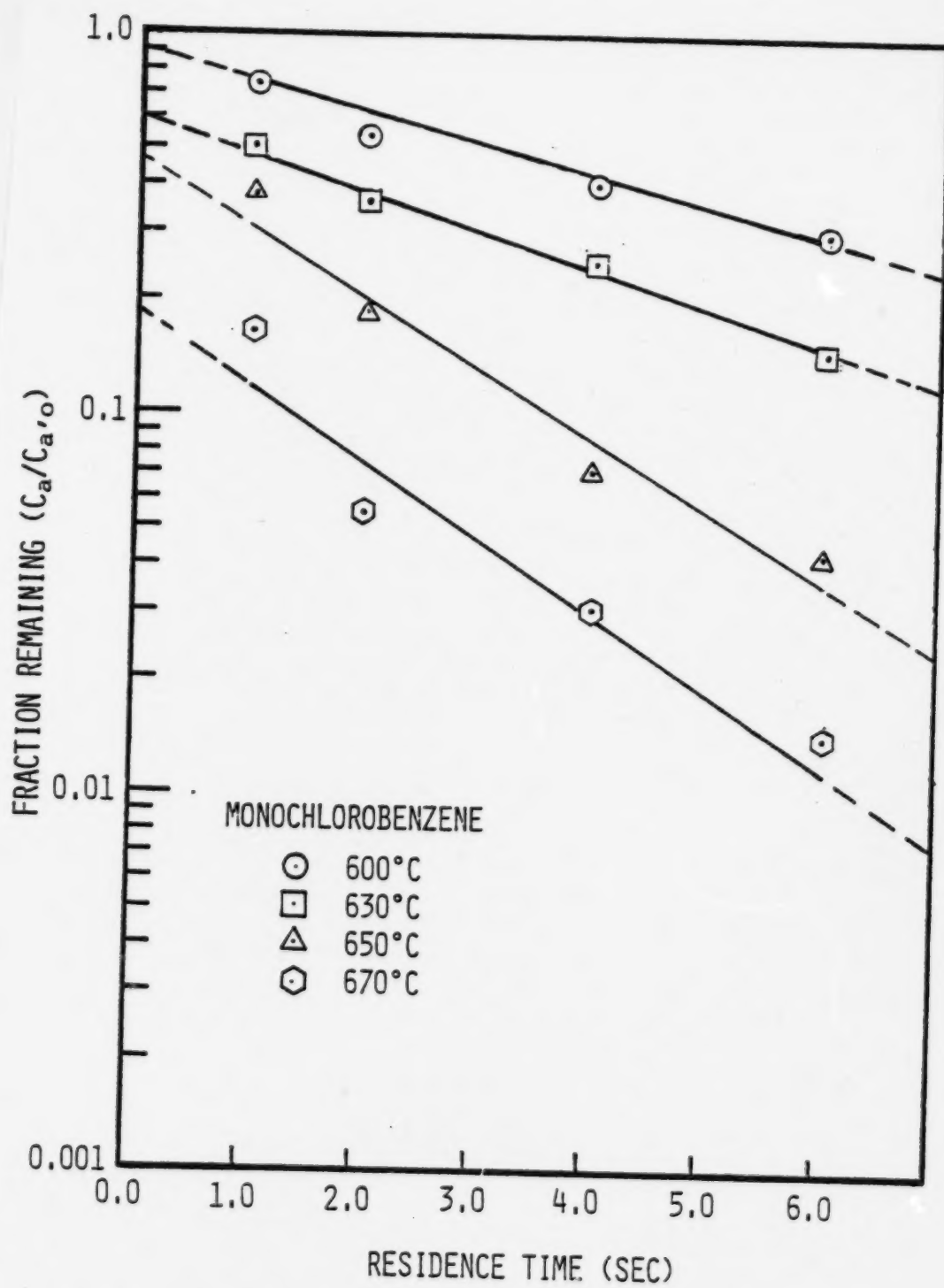
MONOCHLOROBENZENE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r(s)$	Exposure Temperature $T(^{\circ}C)$						
	500	580	600	630	650	670	700
1.0	100		75.5	51.0	37.2	15.7	
2.0	100	78.0	64.2	36.1	17.5	5.50	1.70
4.0	100		40.1	24.8	7.10	3.18	
6.0	100		30.9	15.6	4.26	1.40	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}C)$	Rate Constant $k_1 (s^{-1})$	Correlation Coefficient r^2
600	0.185	0.99
630	0.228	0.99
650	0.424	0.96
670	0.441	0.93
$E_a = 23 \text{ kcal/mole}$ $r^2 = 0.98$ $A = 8.0 \times 10^4 \text{ sec}^{-1}$		



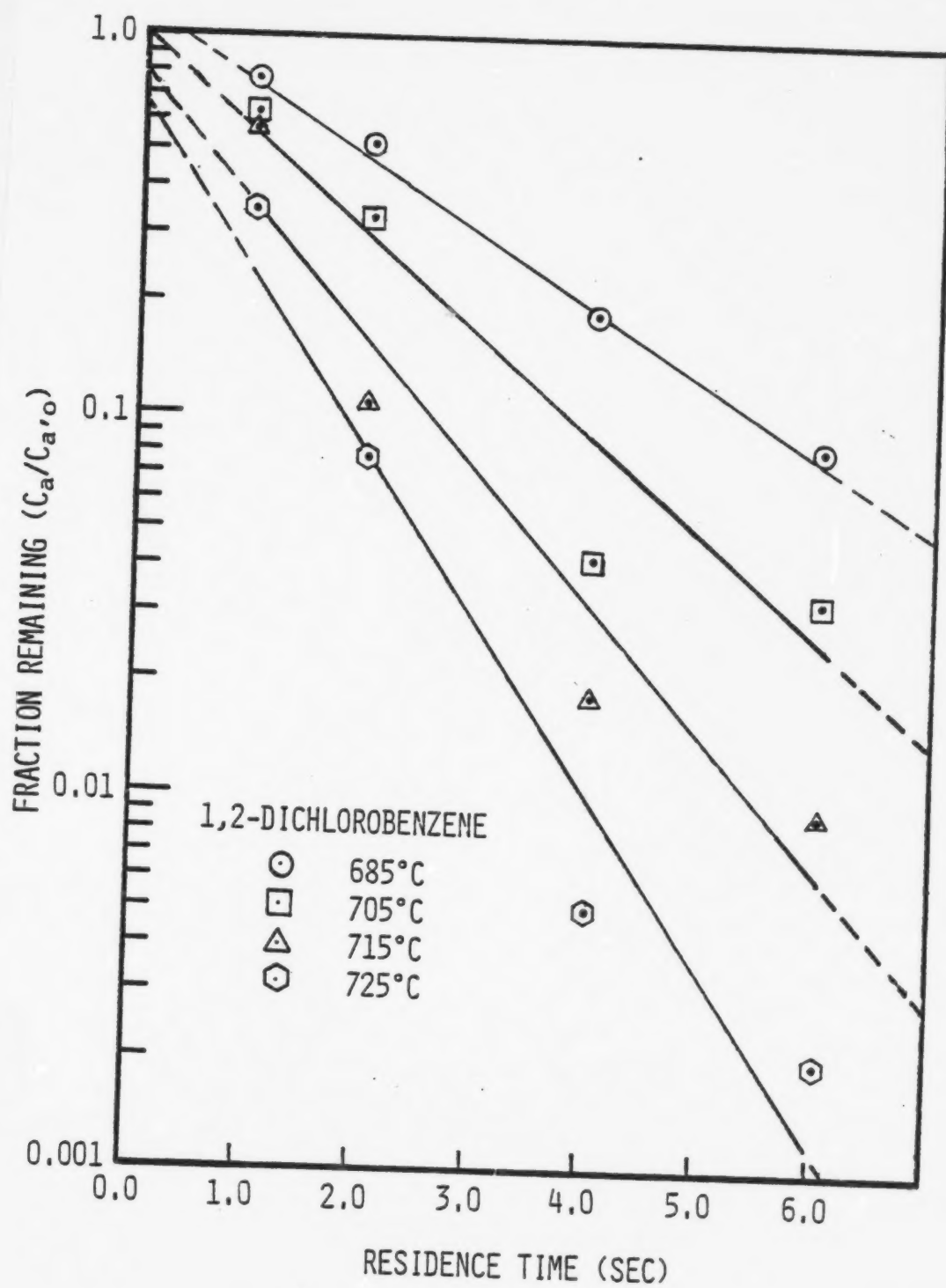
1,2-DICHLOROBENZENE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time t_r (s)	Exposure Temperature $T(^{\circ}\text{C})$						
	600	675	685	705	715	725	740
1.0	100		79.3	64.4	58.8	35.4	
2.0	100	60.2	52.3	33.9	11.3	7.92	0.70
4.0	100		18.3	4.34	1.84	0.53	
6.0	100		8.50	3.82	0.91	0.20	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}\text{C})$	Rate Constant k_1 (s^{-1})	Correlation Coefficient r^2
685	0.456	1.00
705	0.611	0.89
715	0.817	0.92
725	1.05	0.96
$E_a = 39 \text{ kcal/mole}$ $r^2 = 0.97$ $A = 3.0 \times 10^8 \text{ sec}^{-1}$		

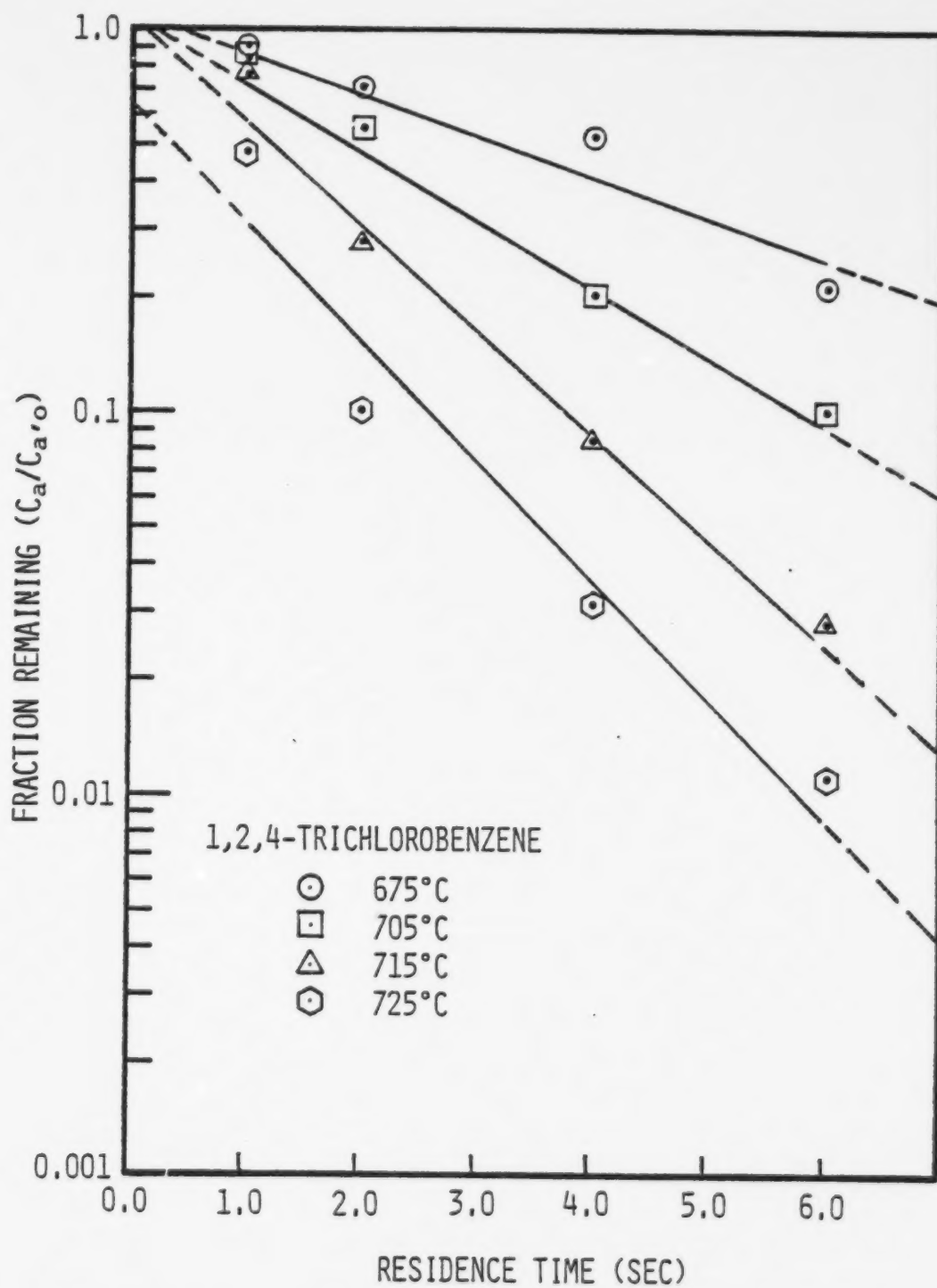


1,2,4-TRICHLOROBENZENE
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	675	705	715	725	740	
1.0	100	90.3	84.5	77.2	49.3	29.5	
2.0	100	71.1	56.2	28.4	10.3	1.62	
4.0	100	53.1	20.4	8.51	3.32		
6.0	100	22.9	10.0	2.80	1.14		

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
675	0.263	0.95
705	0.436	0.99
715	0.646	0.99
725	0.714	0.95
$E_0 = 39 \text{ kcal/mole}$ $r^2 = 0.97$ $A = 2.2 \times 10^8 \text{ sec}^{-1}$		



1,2,3,4-TETRACHLOROBENZENE

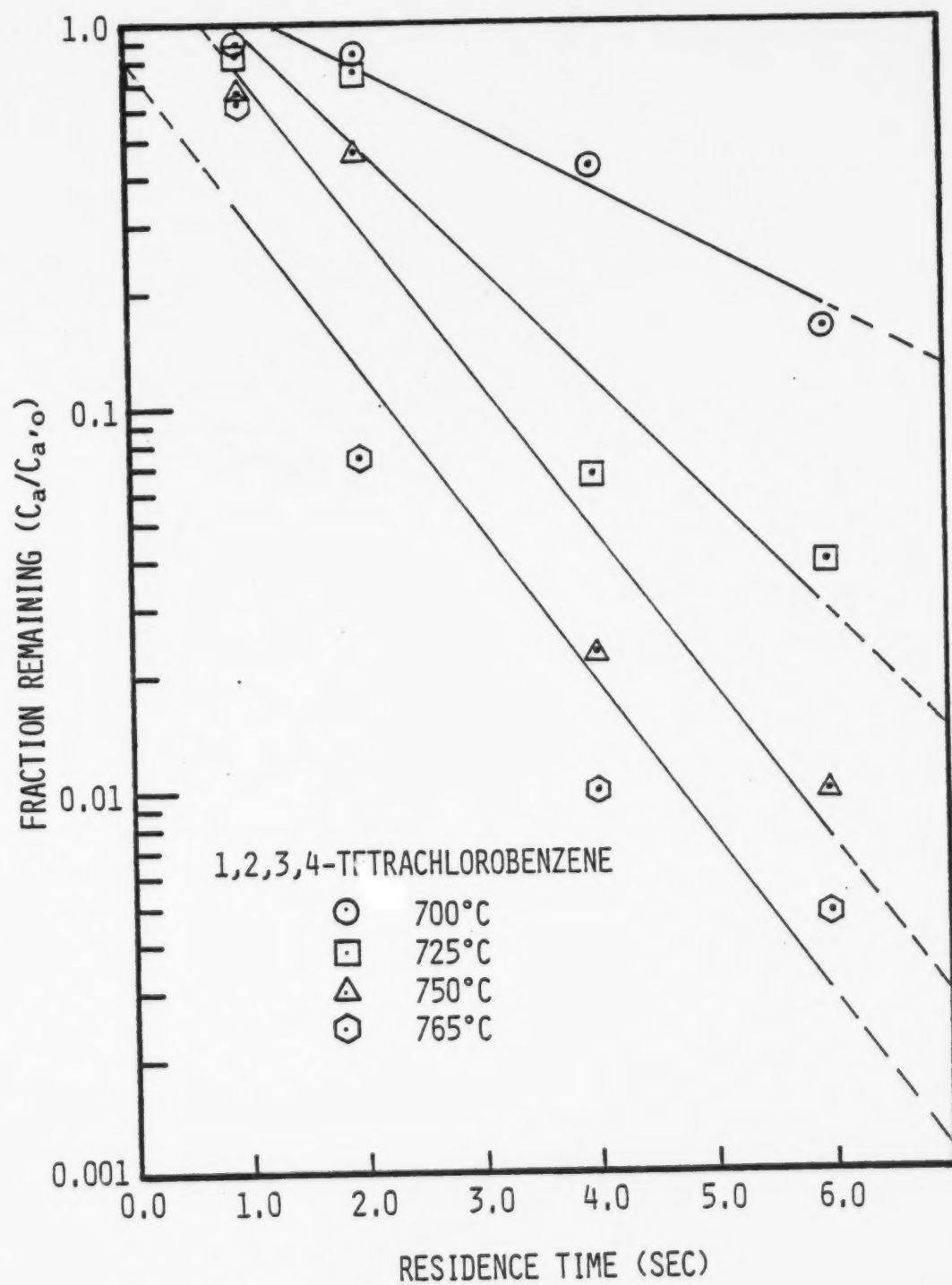
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature $T(^{\circ}\text{C})$						
	300	675	700	725	750	765	780*
1.0			91.9	86.4	69.4	66.3	
2.0	100	90.9	85.4	77.9	47.8	7.53	2.18
4.0			43.6	6.85	2.32	1.06	
6.0			15.5	4.00	1.03	0.49	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}\text{C})$	Rate Constant k_1 (s^{-1})	Correlation Coefficient r^2
700	0.364	0.96
725	0.693	0.92
750	0.926	0.94
765	0.942	0.91
$E_a = 30 \text{ kcal/mole}$ $r^2 = 0.91$ $A = 1.9 \times 10^6 \text{ sec}^{-1}$		

*Additional Data: $T = 800^{\circ}\text{C}$, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.76
 $T = 815^{\circ}\text{C}$, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.42



HEXACHLOROBENZENE

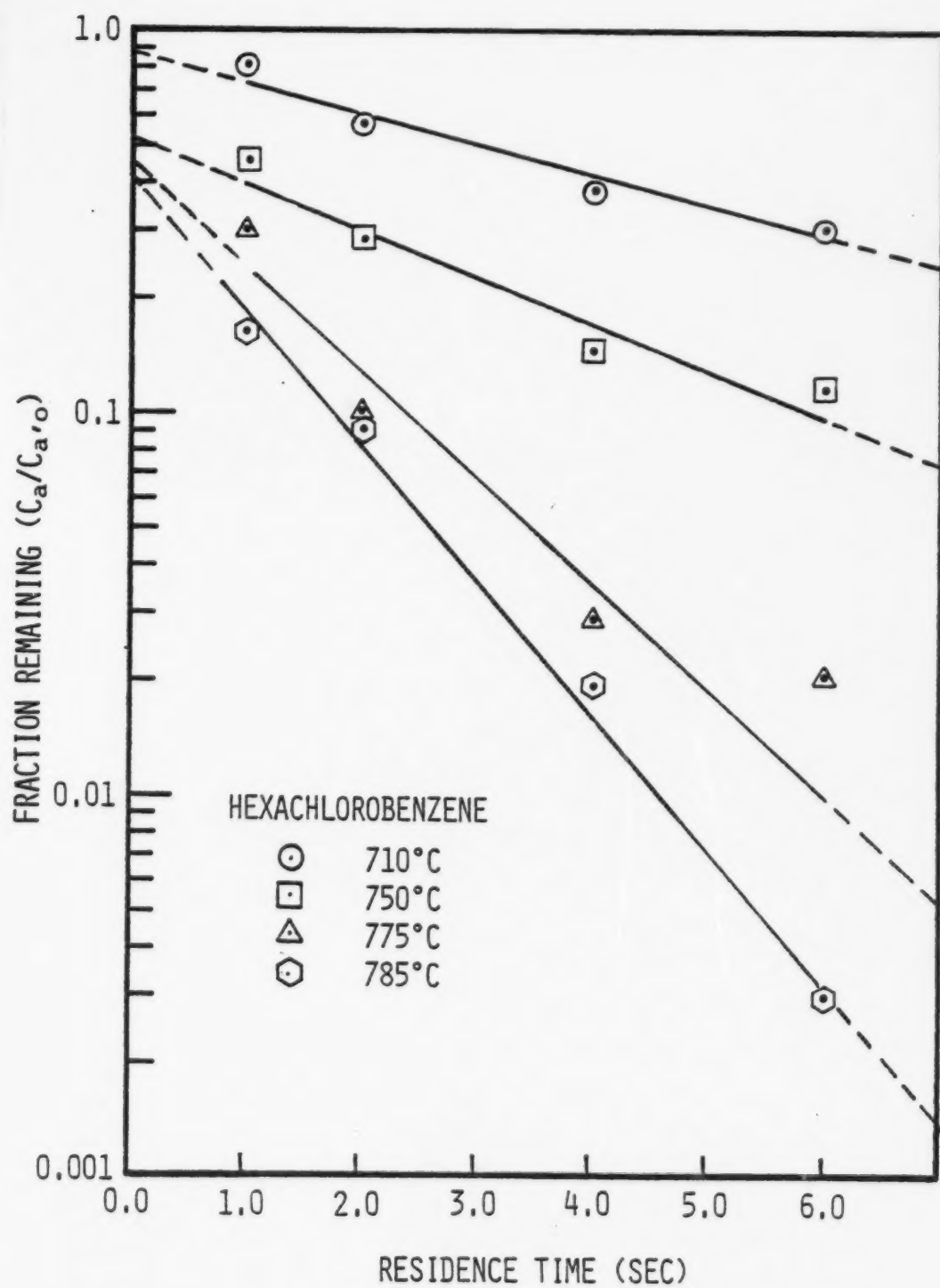
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	650	710	750	775	785	800*
1.0	100	100	81.2	46.0	30.7	16.0	
2.0	100	87.2	58.3	28.6	10.4	9.3	3.32
4.0	100	85.9	38.4	14.2	2.8	1.91	
6.0	100	84.5	31.9	11.3	1.1	0.30	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_i (s ⁻¹)	Correlation Coefficient r^2
710	0.184	0.95
750	0.281	0.94
775	0.651	0.97
785	0.804	0.99
$E_a = 41 \text{ kcal/mole}$ $r^2 = 0.92$ $A = 2.5 \times 10^8 \text{ sec}^{-1}$		

*Additional Data: T=815°C, $\bar{t}_r$ =1.0s, wt. % remaining=9.22
T=830°C, $\bar{t}_r$ =1.0s, wt. % remaining=1.36



PYRIDINE

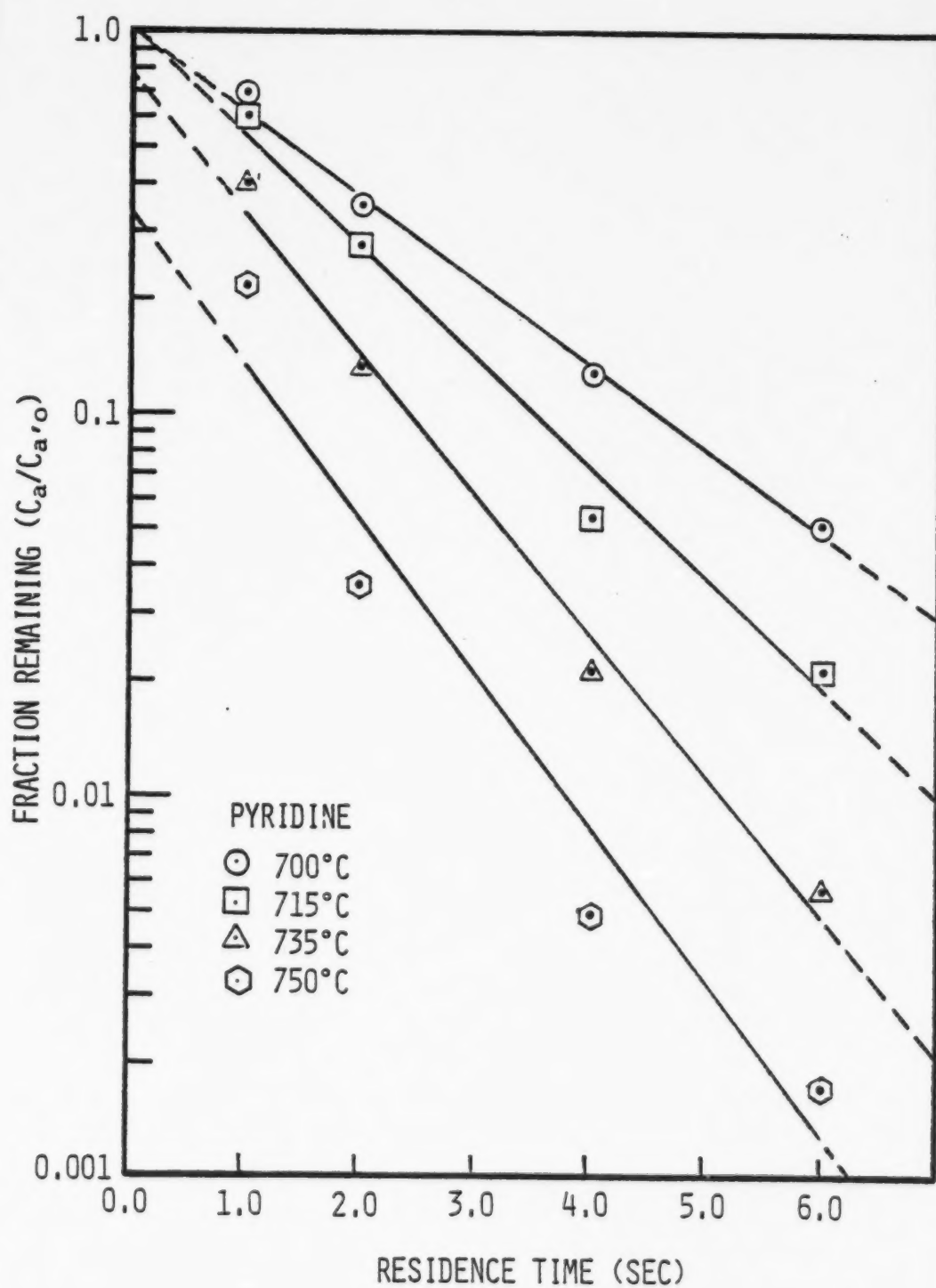
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	650	700	715	735	750	765*
1.0			70.2	61.3	40.4	21.8	
2.0	100	84.6	35.6	27.9	12.8	3.61	1.99
4.0			12.3	5.42	2.10	0.49	
6.0			5.16	2.18	0.57	0.17	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
700	0.518	0.99
715	0.679	0.98
735	0.847	0.98
750	0.946	0.95
$E_a = 24 \text{ kcal/mole}$ $r^2 = 0.97$ $A = 1.1 \times 10^5 \text{ sec}^{-1}$		

*Additional Data: T = 780°C, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.85
T = 800°C, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.18



ANILINE

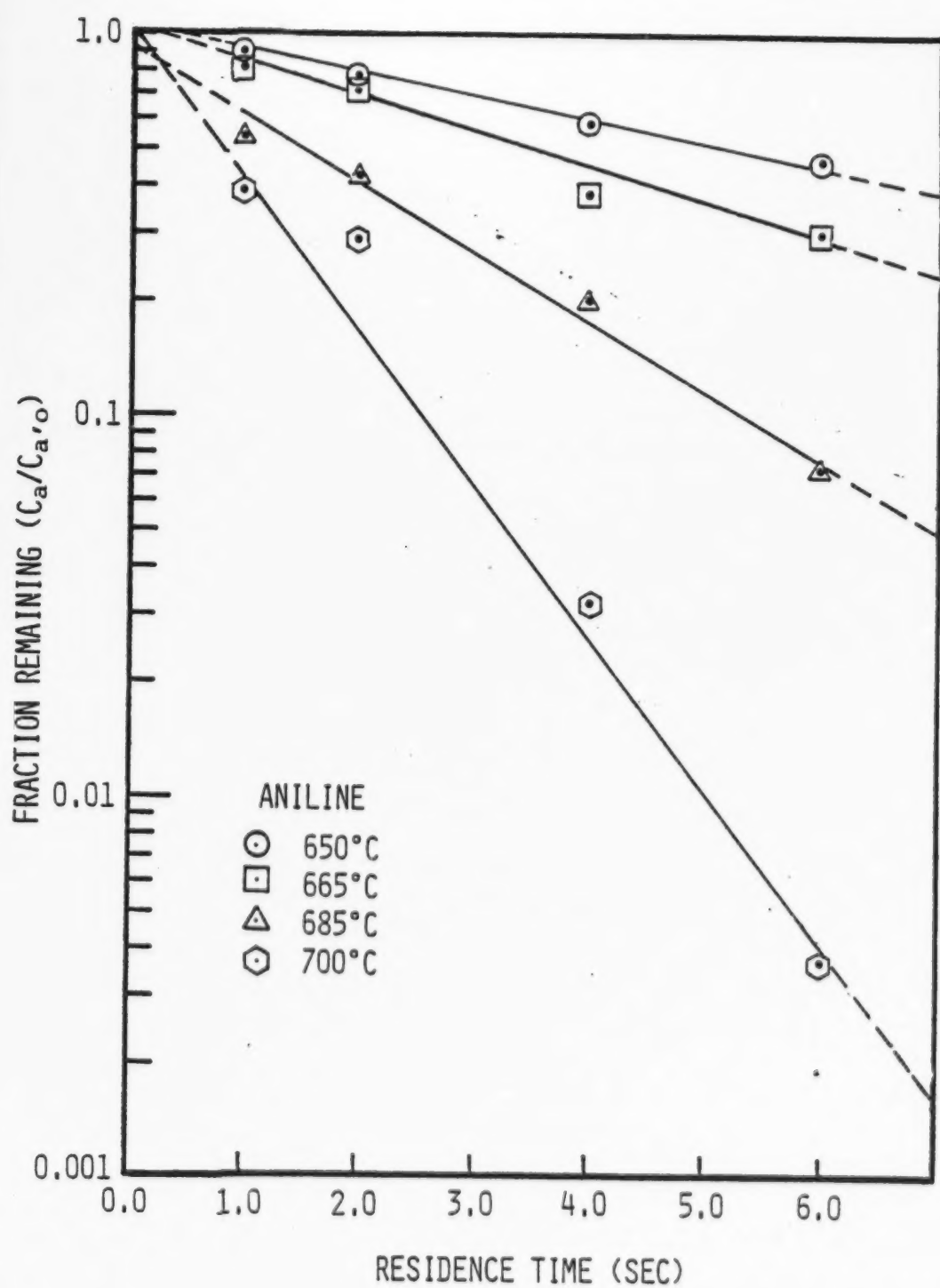
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	650	665	685	700	725	730*
1.0		90.1	82.3	55.1	39.7		
2.0	93.3	78.0	75.4	42.8	29.0	1.20	0.61
4.0		69.6	38.2	20.5	3.30		
6.0		46.7	30.6	7.33	0.36		

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
650	0.123	0.94
665	0.216	0.95
685	0.405	0.99
700	0.977	0.98
$E_a = 71 \text{ kcal/mole}$ $r^2 = 0.98$ $A = 9.3 \times 10^{15} \text{ sec}^{-1}$		

*Additional Data: T = 735°C, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.26



NITROBENZENE

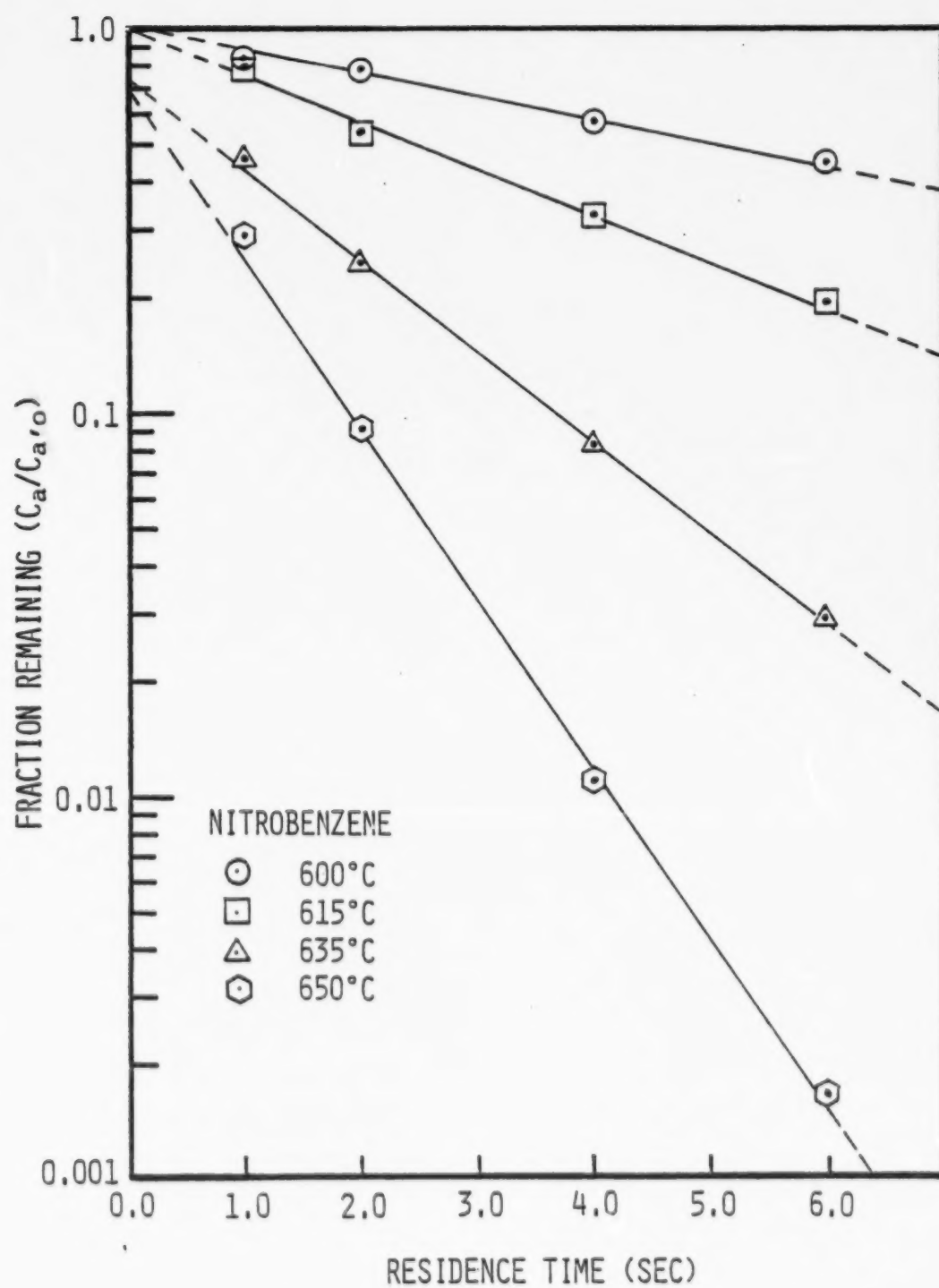
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	475	575	600	615	625	635	650*
1.0			84.4	80.3		45.9	29.2
2.0	100	91.3	79.8	54.0	44.5	24.1	9.03
4.0			58.3	32.8		8.10	1.08
6.0			44.1	19.2		2.88	0.16

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
600	0.135	0.98
615	0.279	0.99
635	0.550	0.99
650	1.039	0.99
$E_a = 64 \text{ kcal/mole}$ $r^2 = 0.99$ $A = 1.4 \times 10^{15} \text{ sec}^{-1}$		

*Additional Data: T = 675°C, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.32



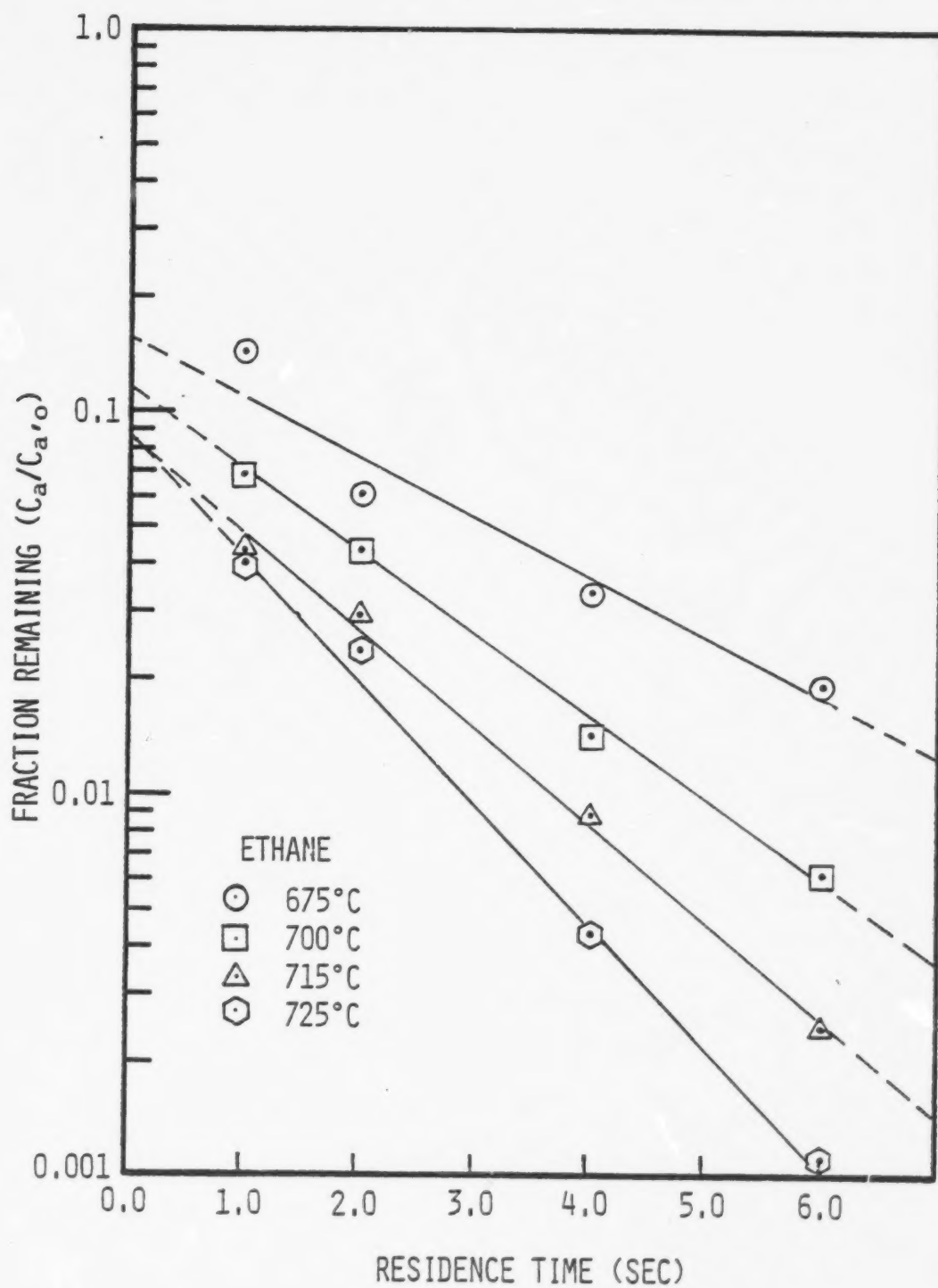
ETHANE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time t_r (s)	Exposure Temperature $T(^{\circ}\text{C})$						
	450	650	675	700	715	725	
1.0	100		14.4	6.99	4.35	4.01	
2.0	100	18.7	6.10	4.33	2.91	2.37	
4.0	100	5.91	3.40	1.40	0.89	0.43	
6.0	100	4.29	1.91	0.61	0.24	0.11	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}\text{C})$	Rate Constant k_1 (s^{-1})	Correlation Coefficient r^2
675	0.377	0.94
700	0.496	0.99
715	0.587	0.99
725	0.739	0.99
$E_a = 24 \text{ kcal/mole}$ $r^2 = 0.97$ $A = 1.3 \times 10^5 \text{ sec}^{-1}$		



1,1,1-TRICHLOROETHANE

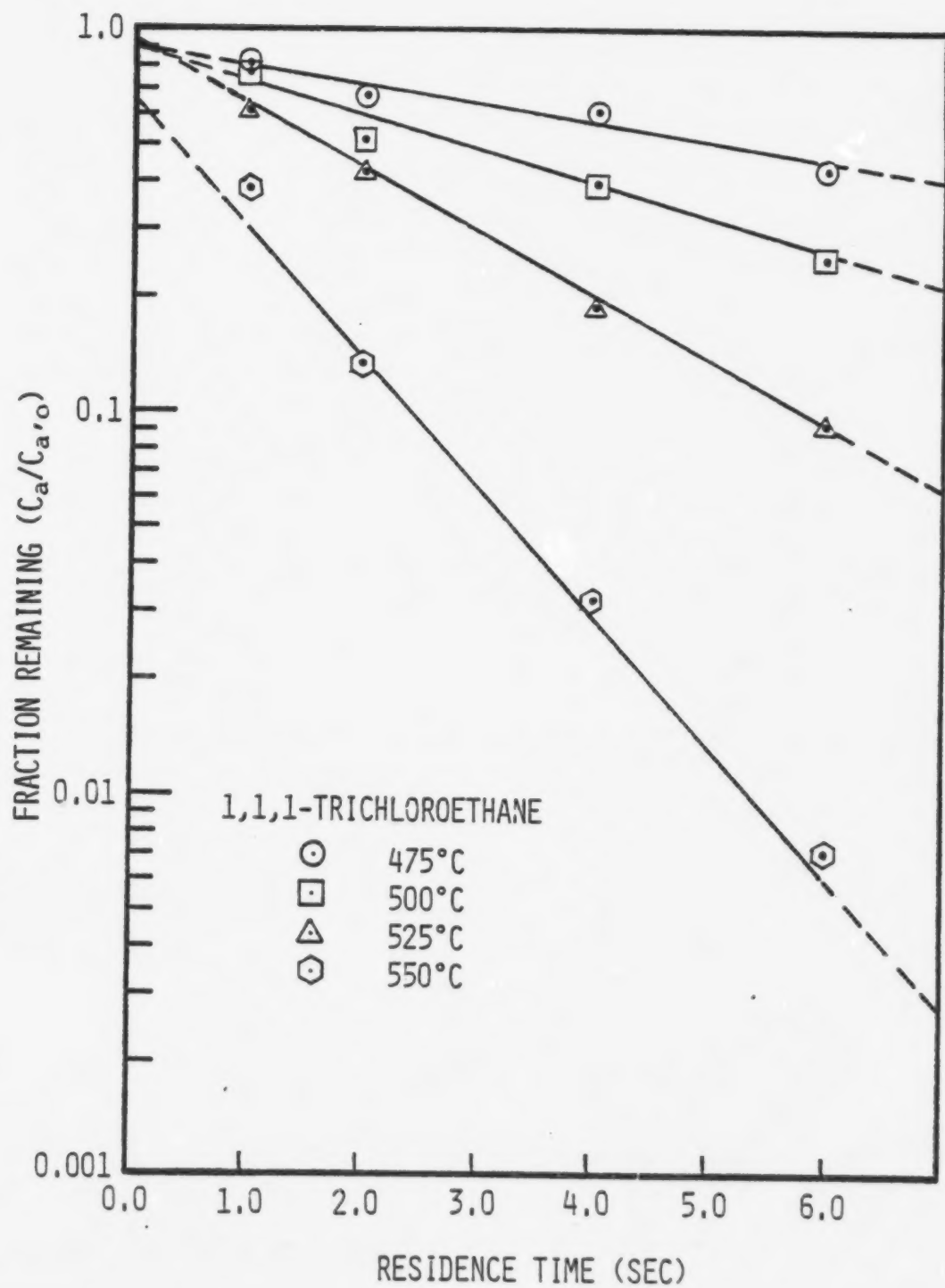
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	350	400	450	475	500	525	550*
1.0			83.8	80.8	78.3	62.9	38.8
2.0	98.3	92.3	79.3	68.1	52.2	42.7	10.3
4.0			62.3	62.2	40.5	18.2	3.20
6.0			51.4	44.3	26.0	9.41	0.63

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
475	0.111	0.94
500	0.205	0.97
525	0.384	1.00
550	0.782	0.98
$E_a = 32 \text{ kcal/mole}$ $r^2 = 1.00$ $A = 1.9 \times 10^8 \text{ sec}^{-1}$		

*Additional Data: T = 575°C, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.87



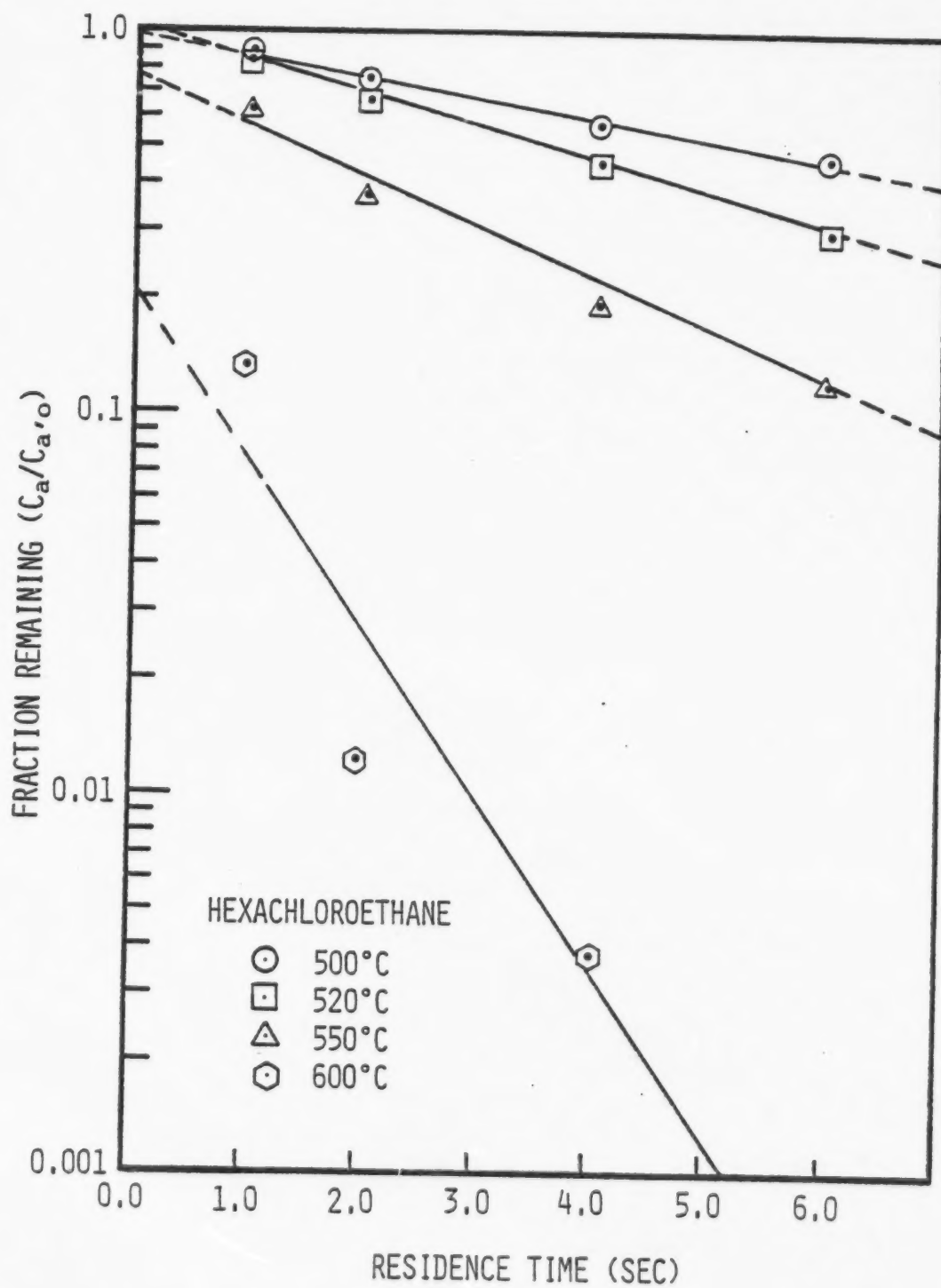
HEXACHLOROETHANE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	400	500	520	550	600	630	
1.0	100	90.0	85.0	62.3	12.69	0.49	
2.0	100	76.5	67.8	37.0	1.19		
4.0	100	59.4	46.8	19.6	0.38		
6.0	100	48.9	31.0	11.9	0.03		

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_t (s ⁻¹)	Correlation Coefficient r^2
500	0.121	0.99
520	0.199	1.00
550	0.324	0.98
600	1.09	0.95
$E_a = 29 \text{ kcal/mole}$ $r^2 = 0.99$ $A = 1.9 \times 10^7 \text{ sec}^{-1}$		



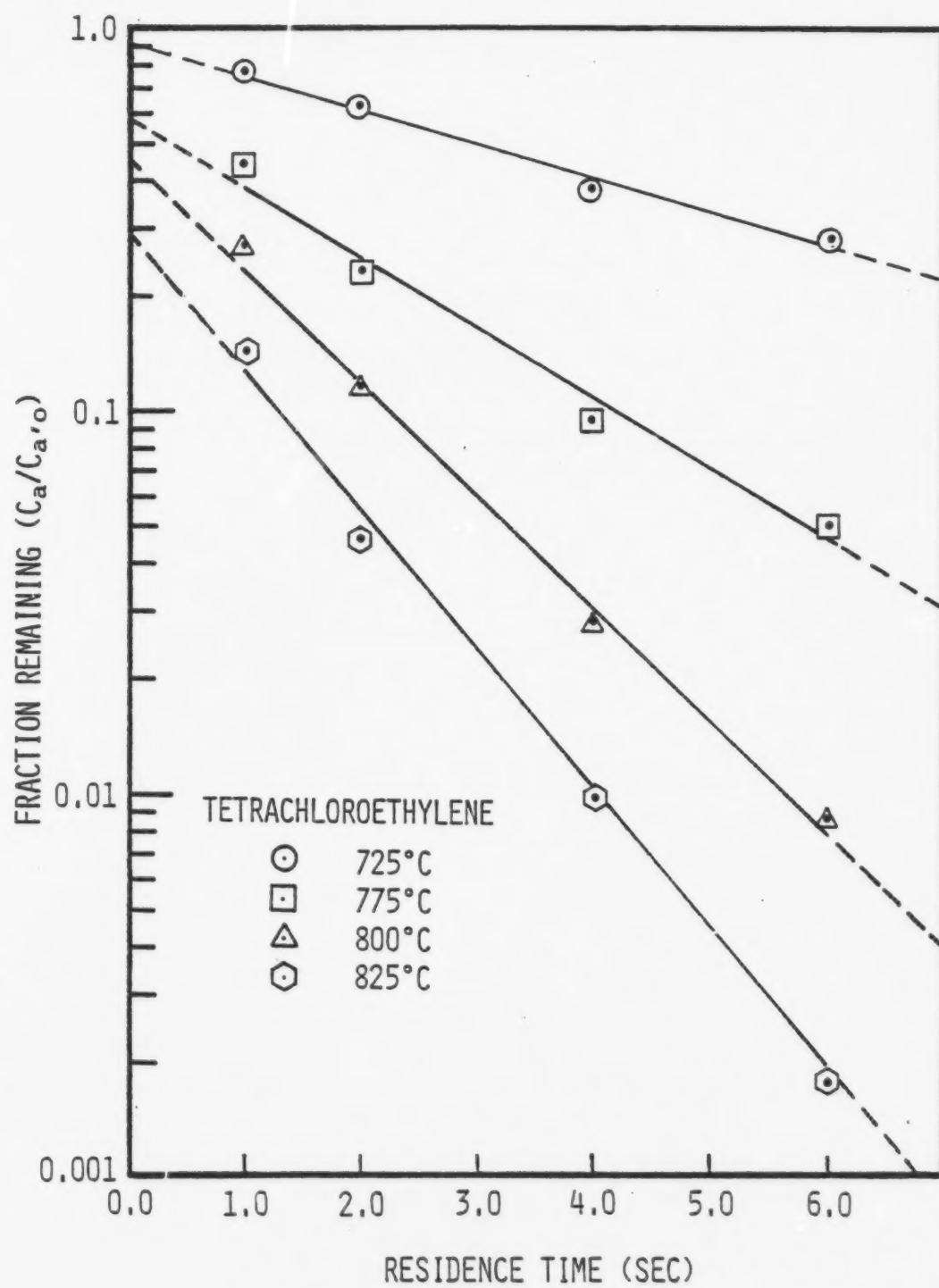
TETRACHLOROETHYLENE

THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time t_r (s)	Exposure Temperature $T(^{\circ}\text{C})$						
	600	675	725	775	800	825	860
1.0	100		78.7	44.1	26.4	13.7	3.72
2.0	100		61.9	23.2	11.2	4.66	0.67
4.0	100		38.4	9.27	2.72	1.00	
6.0	100	74.6	28.8	5.08	0.84	0.16	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature $T(^{\circ}\text{C})$	Rate Constant k_1 (s^{-1})	Correlation Coefficient r^2
725	0.204	0.99
775	0.428	0.98
800	0.685	0.99
825	0.873	1.00
$E_a = 33 \text{ kcal/mole}$ $r^2 = 0.99$ $A = 2.6 \times 10^6 \text{ sec}^{-1}$		



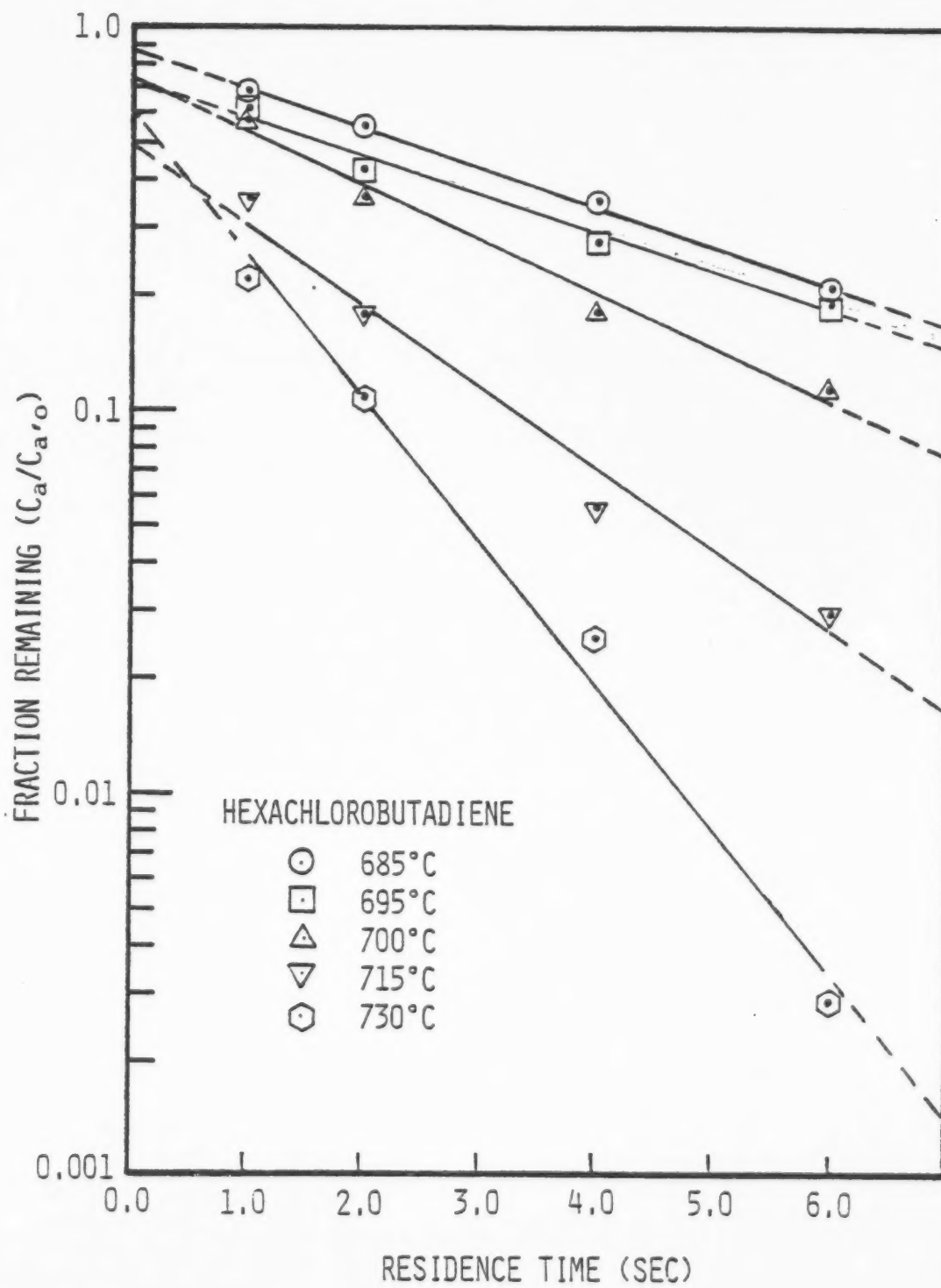
HEXACHLOROBUTADIENE
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	500	650	685	695	700	715	730*
1.0	100		69.5	61.9	57.8	35.1	23.4
2.0	100	73.3	55.2	41.9	36.9	17.1	10.7
4.0	100		35.1	27.5	17.2	5.72	2.48
6.0	100		21.5	18.6	11.0	2.91	0.28

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
685	0.234	1.00
695	0.232	0.98
700	0.333	0.98
715	0.496	0.98
730	0.873	0.99
$E_a = 59 \text{ kcal/mole}$ $r^2 = 0.96$ $A = 6.3 \times 10^{12} \text{ sec}^{-1}$		

*Additional Data: T = 760°C, $\bar{t}_r = 2.0\text{s}$, wt % remaining = 0.01



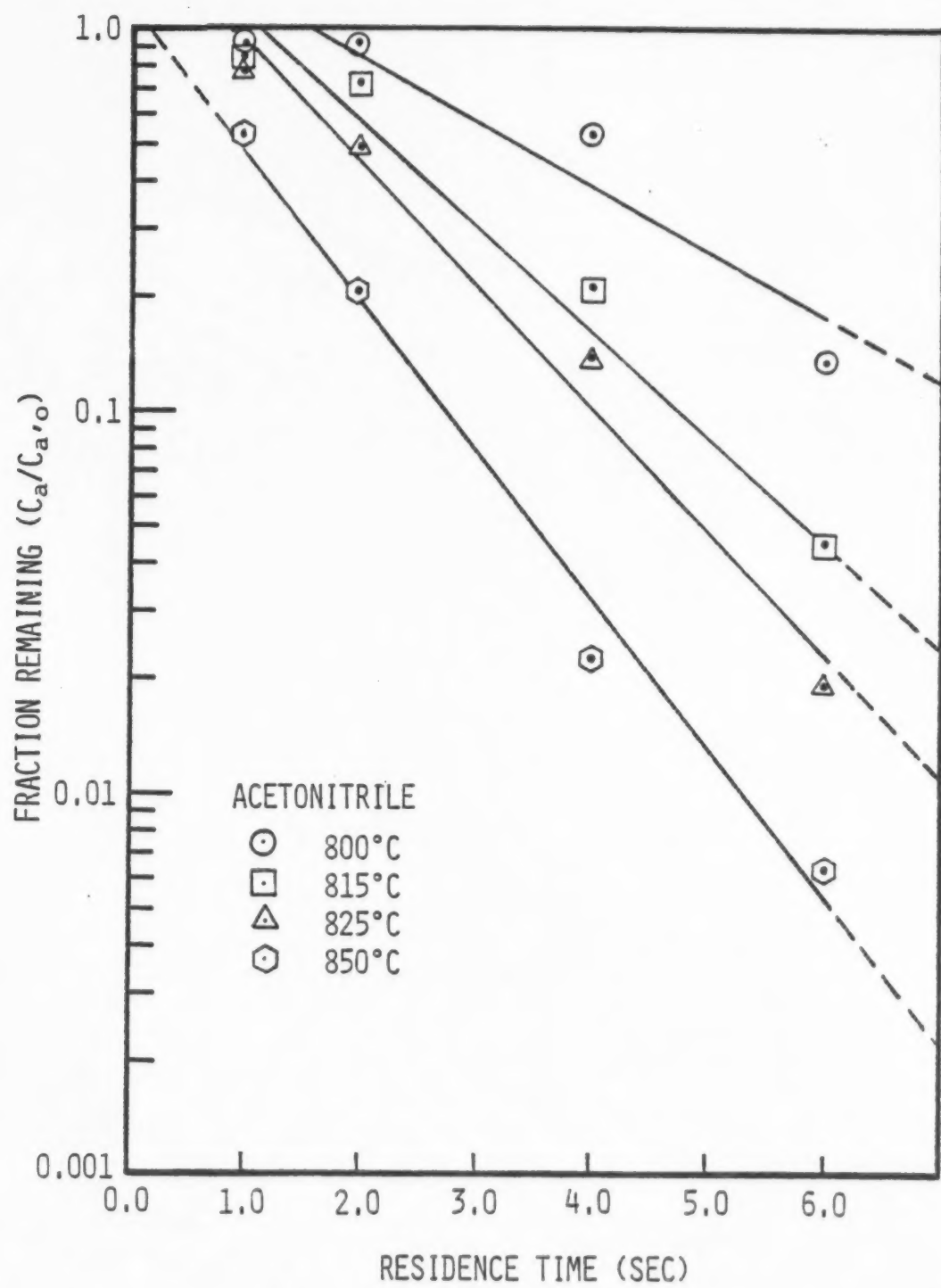
ACETONITRILE
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	775	800	815	825	850	875*
1.0	100		91.8	85.5	78.3	53.1	30.2
2.0	100		91.6	72.8	49.2	21.0	6.46
4.0	100		53.4	21.6	13.2	2.24	
6.0	100	88.2	13.1	4.50	1.97	0.62	

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
800	0.390	0.89
815	0.607	0.97
825	0.738	0.98
850	0.911	0.99
$E_a = 40 \text{ kcal/mole}$		$r^2 = 0.91$
$A = 4.7 \times 10^7 \text{ sec}^{-1}$		

*Additional Data: T = 900°C, $\bar{t}_r = 1.0\text{s}$, wt % remaining = 6.14

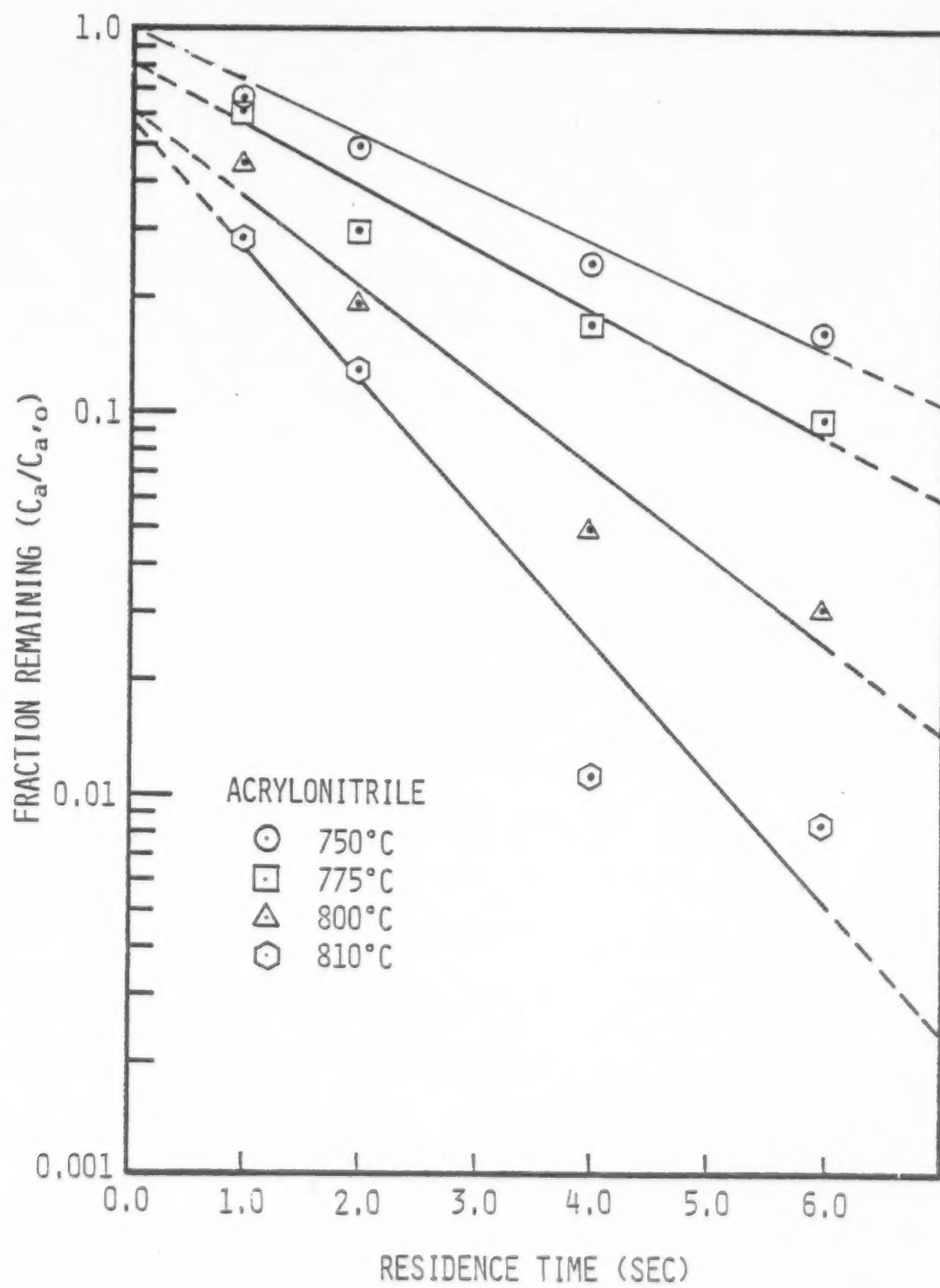


ACRYLONITRILE
THERMAL DECOMPOSITION DATA
(wt % Remaining)

Mean Residence Time $\bar{t}_r$ (s)	Exposure Temperature T(°C)						
	600	750	775	800	810	835	
1.0	100	77.9	72.4	45.5	38.8	2.21	
2.0	100	50.9	30.4	19.9	12.7		
4.0	100	25.1	16.4	5.02	1.12		
6.0		15.4	9.79	3.10	0.84		

FIRST ORDER
KINETIC PARAMETERS

Exposure Temperature T(°C)	Rate Constant k_1 (s ⁻¹)	Correlation Coefficient r^2
750	0.324	0.99
775	0.375	0.93
800	0.543	0.95
810	0.800	0.90
$E_a = 31 \text{ kcal/mole}$ $r^2 = 0.88$ $A = 1.3 \times 10^6 \text{ sec}^{-1}$		



APPENDIX C
COMPILATION OF GLOBAL GAS PHASE OXIDATION RATE DATA

For completeness, we have included a survey of global gas phase oxidation rate data previously reported in the literature for the twenty test compounds. Direct comparison to data which we have generated is difficult for several reasons.

Firstly, the experimental conditions under which the studies were performed vary, ie. different temperature ranges, reaction atmospheres, residence times, etc. Secondly, the data has typically been reduced and presented with different formulations. Thirdly, there is apparently significant scatter in the results when multiple studies on the same compound have been performed, and insufficient data is available from which to make a statistically valid inter-comparison of results.

In order to compare results, it is tempting to extrapolate the data beyond the range reported by the authors and to analyze their data with a common reduction and formulation scheme. This is beyond the scope of this report; furthermore, such practice should be considered risky at best. Some of the reported data was obtained under poorly defined or controlled conditions which could be responsible for the scatter in results. We feel that this further supports the need for obtaining thermal decomposition data under consistent, controlled laboratory conditions such that trends or differences in compound properties can be identified.

Methane

This is a favorite for study by combustion researchers. Global rate expressions for the oxidation of methane are reported in table C.1. The work of Dryer and Glassman is the most frequently quoted and their rate expression is recommended by most researchers. When their rate expression is evaluated at $[O_2] = 9.38 \times 10^{-6}$ mole/cm³ (21% v/v), values are obtained for A and E_a of 1.5×10^9 s⁻¹ and 48.4 kcal/mole, respectively. These compare favorably with our values of 3.5×10^9 s⁻¹ and 48 kcal/mole. Plots of the predicted initial decomposition rate as a function of temperature for a given initial concentration of methane is presented in Figure C.1, for our work, the work of Dryer and Glassman, and the work of Lee which was discussed in the text. It may be seen from the plot that the results of all three studies are in approximate agreement.

TABLE C.1. GLOBAL KINETIC DATA FOR METHANE

RATE EXPRESSION	TEMPERATURE RANGE (°C)	INVESTIGATORS
$\frac{-d[CH_4]}{dt} = 7 \times 10^8 [CH_4]^{-0.5} [O_2]^{1.5} T^{-1} e^{-60,000/RT}$ mole/cm ³ -sec	925-1125	Kozlov, 1969, (35)
$\frac{-d[CH_4]}{dt} = 6 \times 10^{10} [CH_4]^{-0.4} [O_2]^{1.4} e^{-57,000/RT}$ mole/cm ³ -sec	>925	Nemeth and Sawyer, 1969, (36)
$\frac{-d[CH_4]}{dt} = 5.3 \times 10^{15} F_{CH_4}^{0.5} F_{O_2}^{0.5} (P/RT)^2 e^{-57,000/RT}$ mole/l-sec, F=mole fraction, and P/RT is in mole/l	1175-1477	Williams et. al., 1969, (37)
$\frac{-d[CH_4]}{dt} = 10^{13.2} [CH_4]^{0.7} [O_2]^{0.8} e^{-48,400/RT}$	825-1125	Dryer and Glassman, 1973, (38)
$\frac{-d[CH_4]}{dt} = 1.7 \times 10^{11} [CH_4] e^{-52,100/RT}$	~650- 800	Lee, et. al., 1982, (22)
$\frac{-d[CH_4]}{dt} = 3.5 \times 10^9 [CH_4] e^{-48,000/RT}$	700- 800	UDRI

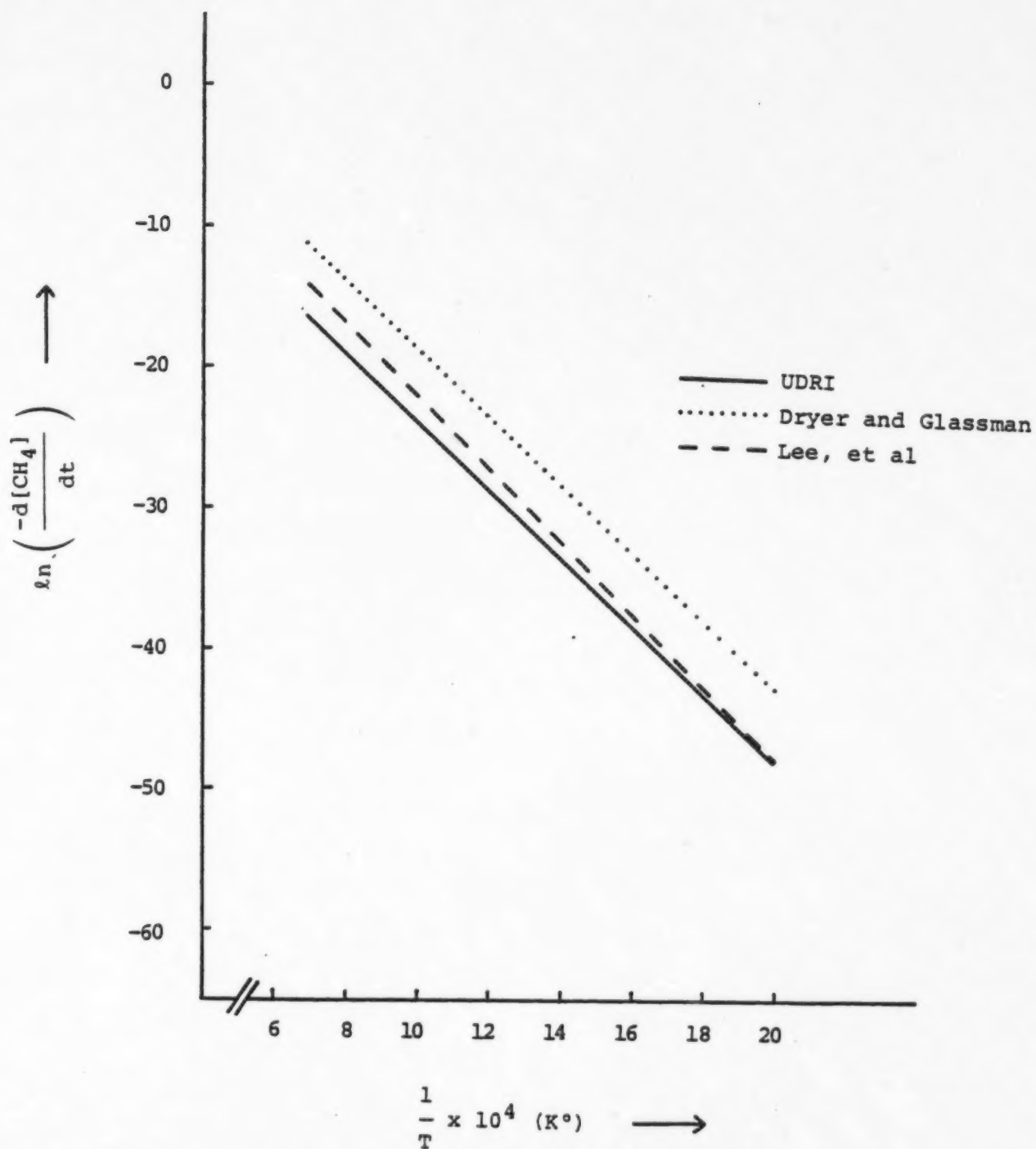


Figure C.3. Initial Rate of Decomposition of Methane as a function of Temperature (K°) for $[CH_4]_0 = 10 \text{ ppm}$ and $[O_2] = 21\% \text{ (v/v)}$.

Ethane

Glassman, Dryer, and Cohen (39) have also investigated the decomposition of ethane in the presence of an excess of oxygen. Their reported rate expression,

$$\frac{-d[C_2H_6]}{dt} = 10^{7.18} [C_2H_6]^{0.8} e^{-72,900/RT}$$

was obtained over the temperature range 625°C to 775°C. Our data was obtained over the temperature range 675°C to 725°C yielding a pseudo first order rate expression

$$\frac{-d[C_2H_6]}{dt} = 1.3 \times 10^5 [C_2H_6] e^{-24,000/RT}$$

The composition of the reaction atmosphere is not known for the work of Glassman, Dryer, and Cohen, while our data was obtained in flowing air.

Clearly, the frequency factors and activation energies show significant disagreement. This is of course affected by the fact that the reaction order with respect to ethane has been fit to 0.8 for the work of Glassman, Dryer, and Cohen. In our work, the data was fit to first order. Lee et al., (22) reported first order Arrhenius parameters of 63.6 and 5.7×10^{14} for E_a and A, respectively. Clearly significant disagreement exists among the three studies and apparent difficulties exist in modeling the decomposition of ethane through a global approach. In spite of these problems, it is evident from Figure C.2 that our results are in moderate agreement with that of Dryer and Glassman while the results of Lee exhibit significant differences.

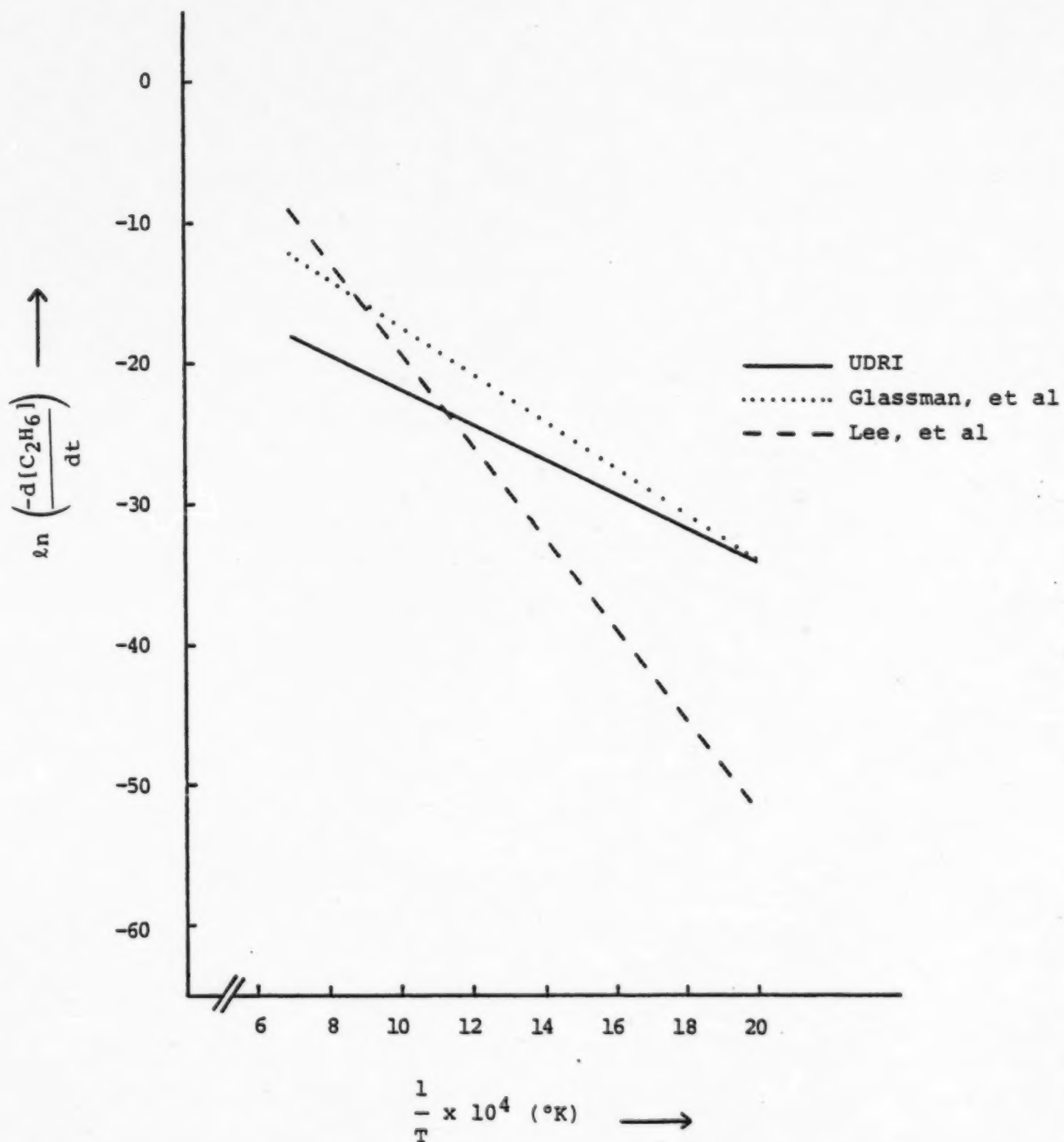


Figure C.2. Initial Rate of Decomposition of Ethane as a Function of Temperature ($^\circ\text{K}$) for $[C_2H_6]_0 = 10$ ppm and $[O_2] = 21\%$ (v/v).

Benzene

Global decomposition data for the oxidation of benzene have been obtained by Seshadri and Williams (40) and Fujii and Asaba (41). The latter study is recommended by the NBS.

Seshadri and Williams' data is based on second order kinetics and quotes an activation energy of 36 kcal/mole and frequency factor of 6.0×10^{14} cm³/mole-sec. The precise reaction atmosphere used in their study is not known. Fujii and Asaba studied oxidations and pyrolysis under a range of conditions using shock tubes techniques. Their rate expression for benzene oxidation

$$\frac{-d[C_6H_6]}{dt} = 10^{14.0} [C_6H_6]^{0.9 \pm 0.3} [O_2]^{0.9 \pm 0.2} e^{-35 \pm 5/RT}$$

was obtained over the range of 1077-1227°C. For an atmosphere of 21% O₂ this corresponds to an apparent pseudo-first order frequency factor of 9.38×10^8 s⁻¹ and an activation energy of 35 kcal/mole. This may be compared to our pseudo first order parameters of 2.8×10^8 s⁻¹ and 38 kcal/mole and to those of Lee, et al. (22) of 7.4×10^{21} s⁻¹ and 95.9 kcal/mole.

Our results are compared with that of other studies in Figure C.3. The results of Fujii and Asaba are seen to be in moderate agreement with our results while the results of Lee show significant disagreement.

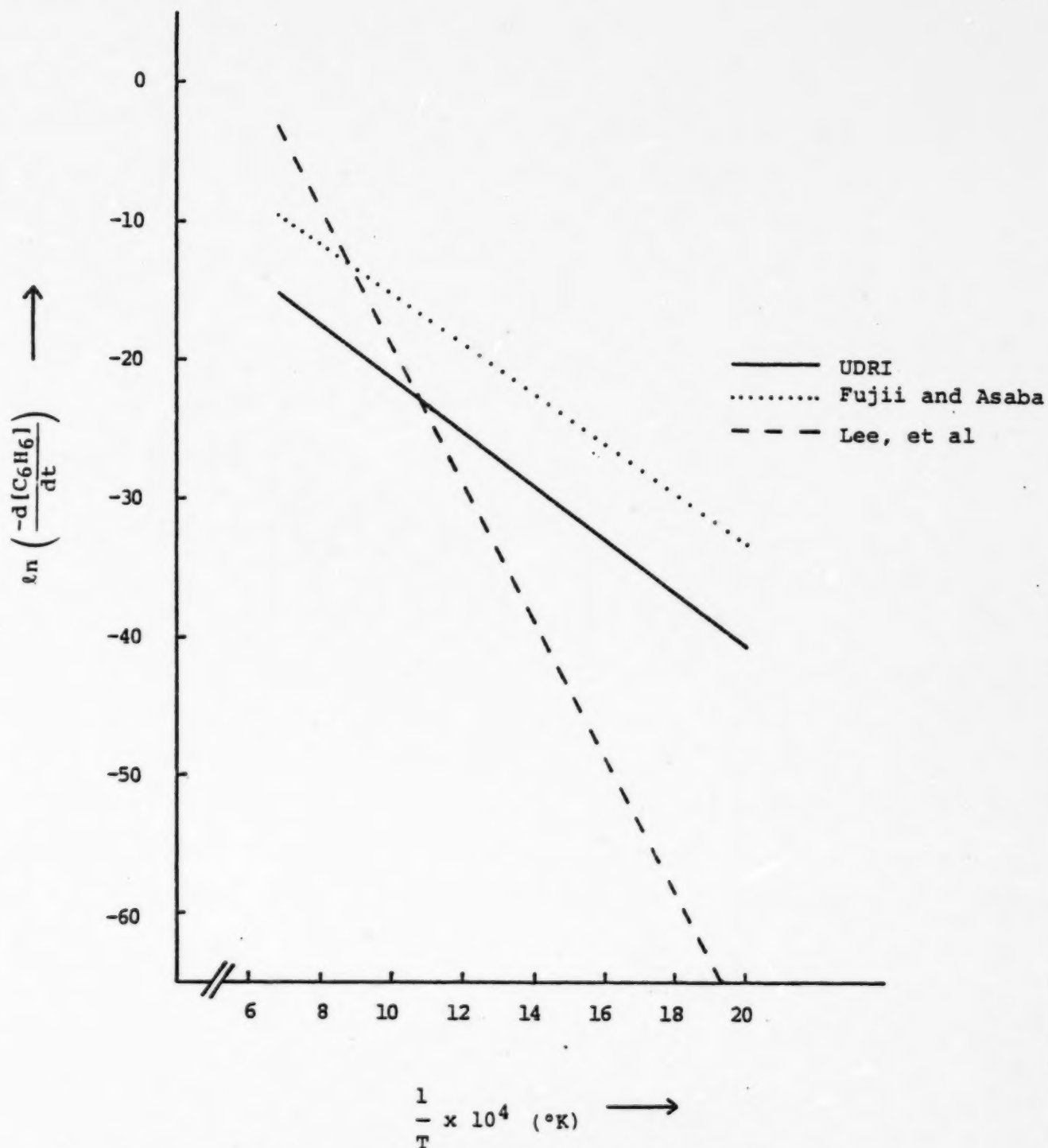


Figure C.3. Initial rate of decomposition of Benzene as a function of temperature ($^\circ\text{K}$) for $[C_6H_6]_0 = 10 \text{ ppm}$ and $[O_2] = 21\% \text{ (v/v)}$.

APPENDIX D
COMPARISON OF LABORATORY AND FIELD DATA

CASE 1

HEX WASTES

Lab Study

Major constituents of hex waste sample were determined to be hexachlorocyclopentadiene (HCCPD), octachlorocyclopentene (OCCP), hexachlorobenzene (HCBz), and pentachlorobenzene (PCBz). HCBz was determined to be a major PIC and was predicted to be the most stable species in the system requiring a temperature greater than 900°C at $t_r = 2s$ to achieve 99.99% DE. HCCPD and OCCP were predicted to have a 99.99% DE at temperatures less than 800°C and 600°C respectively at $t_r = 2s$.

Reference: "High-Temperature Degradation Characteristics of Hazardous Organic Wastes - A Laboratory Approach", UDRI Draft Report under EPA Grant #R805117-01-0, 1980.

Field Study

Sewage sludge samples from the Morris Forman Wastewater Treatment Plant in Louisville, Kentucky, were determined to contain HCCPD and OCCP as major toxic components along with HCBz and PCBz in somewhat lesser concentrations. Sludge samples were subjected to the pilot scale wet oxidation process at Zimpro Corporation in Rothschild, Wisconsin. The filter cake from the wet oxidation was then incinerated at the Colorado School of Mines in Golden, Colorado (multiple hearth).

OCCP could not be detected in any stack gas samples while HCCPD was detected in trace quantities which corresponds to the predictions of the laboratory study. HCBz and PCBz were the only toxic organics present at measurable levels and HCBz was determined to be the major species in the stack effluent. This is consistent with the lab study on the sludge and subsequent lab studies on pure compounds which have shown PCBz and HCBz to have extreme thermal stability and HCBz to be frequently formed as a product of incomplete combustion.

Reference: "Region IV Support at Morris Forman Wastewater Plant, Louisville, Kentucky," Draft Final Task Report under EPA Contract 68-02-2618, F. C. Whitmore, R. L. Durfee, and M. N. Khattak, Versar, 1977.

CASE 2
p,p'-DDT

Lab Study

Predicted a 99% DE at $T = 480^{\circ}\text{C}$ and a 99.99% DE at $T = 500^{\circ}\text{C}$ for $t_r = 1\text{s}$. Destruction dependent upon residence time. Predicted formation of o,p'-DDT, p,p'-DDE, and o,p'-DDE as major PICs, each more thermally stable than the parent p,p'-DDT. DDD was observed as a thermally stable impurity in the DDT. The most stable of these was p,p'-DDE with a predicted 99.99% DE of 820°C o,p'-DDE had about the same $T_{99.99}$. Thus the DDE isomers were predicted as limiting the incineration.

Reference: "Laboratory Evaluation of High-Temperature Destruction of Kepone and Related Pesticides", EPA-600/2-76-299, D. S. Duvall and W. A. Rubey, 1976.

Field Study

Test burn conducted on 76.2 cm diameter pilot multiple hearth furnace with afterburner at Envirotech Corporation in Brisbane, California. The major reported PICs were the DDE isomers along with some DDD. The average DRE (which included production of DDE and DDD) at 760°C and 955°C was 99.98% with the production of DDE representing the controlling factor in the complete incineration of DDT. Gas phase afterburner non-flame residence times were not available.

Full-scale test burn was conducted at the Palo Alto Incineration in Palo Alto, California. The incineration was similar to that used for the pilot burn but much larger. DDE was again found to be the major PIC and was the limiting factor in the incineration efficiency. The average DRE (again including PICs) was determined to be 99.97 at an average temperature of 678°C .

Reference: "A Study of Pesticide Disposal in a Sewage Sludge Incinerator", Final Report under EPA Contract 68-01-1587, F. C. Whitmore and R. L. Durfee, Versar, 1974.

CASE 3

PCB

Lab Study

Several PCB isomers were studied, results of which are summarized.

<u>Name</u>	<u>$\bar{t}_r$</u>	<u>T₉₉</u>	<u>T_{99.99}</u>
2,5,2',5'-tetrachlorobiphenyl	2.0	745	760
2,5,2',4',5'-pentachlorobiphenyl	2.0	740	760
2,6-dichlorobiphenyl	2.0	800	830
2,2',4,4',5,5'-hexachlorobiphenyl	1.0	720	740
decachloro-biphenyl	1.0	770	820

Numerous PICs were found which included other PCB isomers, chlorinated benzenes, and chlorinated benzofurans. Hexachlorobenzene was a significant product and represented the most stable compound produced by thermal degradation of PCBs, needing about 900°C to be decomposed to 99.99% DE.

References: "Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds", EPA-600/2-77-228, D. S. Duvall and W. A. Rubey, 1977.

"High-Temperature Degradation Characteristics of Hazardous Organic Wastes - A Laboratory Approach", UDRI Draft Report under EPA Grant R805117-01-0, 1980.

Field Study

Full-scale burn conducted at contract disposal facility operated by Rollins Environmental Services, Inc. in Deer Park, Texas. System consisted of rotary kiln and liquid injection burner feeding a common afterburner. The afterburner was operated at a gas temperature of 1300°C with $\bar{t}_r = 2-3s$ and O₂ concentrations of about 10%. DREs of 99.999% were achieved under these conditions which is consistent with laboratory results. Chemical analysis was for the most part conducted by chemical class, thus direct PIC comparison is difficult. Significantly, however, chlorinated benzofurans were detected in the effluent as predicted by the lab studies.

References: "Destroying Chemical Wastes in Commercial-Scale Incinerator Facility Report #6", Rollins Environmental Service Incorporated, Deer Park, Texas, TRW Report, PB-270 897, 1977.

"Incineration of Chemical Wastes Containing Polychlorinated Biphenyls", Assessment of the tests conducted at Rollins Environmental Service, Deer Park, Texas and Energy Service Company, El Dorado, Arkansas, Presented at 182nd National ACS Meeting NY, NY by T. O. Tiernan, et al., 1981.

CASE 4

KEPONE

Lab Study

Predicted a 99% DE at $T = 470^{\circ}\text{C}$ and 99.99% DE at $T \sim 500^{\circ}\text{C}$ for $\bar{t}_r = 1\text{s}$. Residence time dependent. Hexachlorocyclopentadiene and hexachlorobenzene (HCBz) predicted as PICs with HCBz still present at 900°C which would represent limit on incineration.

Reference: "Laboratory Evaluation of High-Temperature Destruction of Kepone and Related Pesticides", EPA-600/2-76-299, D. S. Duvall and W. A. Rubey, 1976.

Field Study

Pilot scale burn conducted at Midland Ross, Surface Combustion Division in Toledo, Ohio. Consisted of rotary kiln pyrolizer and fume incinerator (afterburner). Results indicated at $\bar{t}_r = 2\text{s}$ and $T = 1093^{\circ}\text{C}$ that >99.99% DRE was achieved at all Kepone feed rates. Furthermore, HCBz was detected as the major PIC and was far more stable than Kepone. Thus, HCBz formation was the limiting factor in Kepone incineration.

Reference: "Kepone Incineration Test Program", EPA-600/2-78-108, B. A. Bell and F. C. Whitmore, 1978.